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DIAGRAM OF THE Ni-O_2 SYSTEM AND THE PHYSICO-CHEMICAL NATURE OF THE SOLID PHASE IN THIS SYSTEM

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The objective of this research was the experimental and theoretical study of the diagram of the $Ni - O_2$ system and, in particular, the solving of several unclear problems concerning the existence of various oxygen compounds of nickel, the conditions governing their formation, and a study of their principal physical and chemical properties.

The following investigations were undertaken to settle these problems. The physico-chemical nature of the various phases in the nickel-oxygen system was explored by various methods; what chemical compounds and phases of transitory composition exist in this system were determined; and the physicochemical conditions for their formation and recovery were investigated. The process of isobaric thermal dissociation of various oxygen compounds of nickel and of their solid solutions were studied by the differential thermographic method [1]. An investigation was made of the oxygen compounds of nickel and of their solid solutions by the method of solubility isotherms, as well as by densimetric and magnetometric methods. The structure of the various phases in the nickel-oxygen system was investigated by means of X-rays. The kinetics and reaction equilibrium of the reduction of nickel oxides and of their solid solutions by various reducing agents were explored by various methods. These experimental researches yielded the fundamental thermodynamic functions and characteristics of nickel protoxide, which is of very great practical value in industry.

Some Research Results

Of the various nickel oxides described in the literature, totaling over 25, the existence and conditions for the production of only three have been established: nickel dioxide, NiO_2; nickel sesquioxide, Ni_2O_3; and nickel protoxide, NiO. These three oxides form a series of solid solutions of varying composition with one another, which the authors who discovered them called different nickel oxides [2]. Nickel dioxide is produced by dehydrating the hydrate of this oxide by heating it under high air pressure, or in the cold in vacuum in the presence of phosphoric anhydride. The hydrate of nickel dioxide has been prepared by oxidizing the hydrate of nickel protoxide, freshly precipitated from the nitrate solution by alkali, with bromine. Nickel dioxide is a black amorphous substance.

Nickel sesquioxide was prepared by dehydrating nickel nitrate and keeping it in air at 250° for an extremely long time until it reached constant weight, as well as by keeping nickel dioxide in air at 200°. Nickel sesquioxide is a black powder.

Nickel protoxide was prepared by the prolonged calcining in air, at temperatures above 1100° until constant weight was reached, of solid solutions of nickel oxides, formed by the dehydration and subsequent dissociation of nickel nitrate in air in the temperature range 300-1000°. Nickel protoxide is a powder with a bright light-green color.

The solid solutions of the nickel oxides are powders of various colors, depending upon the temperature at which they are produced.

The solid solution of the nickel oxides produced at a temperature of 300-350° is dark gray, gradually turning into light gray as the temperature is raised to 400-500°. The solid solutions produced at 600° are grayish green. As the temperature is raised still higher, they gradually turn green, becoming lighter and lighter in color, until they change from grayish-green to pure green at a temperature of 900-1000°, approaching the bright, light-green color of pure nickel protoxide, produced by roasting the solid solutions at temperatures in excess of 1100°.

It is extremely hard to prepare pure nickel dioxide or nickel sesquioxide. When aqueous nickel dioxide is dehydrated, it begins to dissociate when only slightly heated, in accordance with the equation:

$$2NiO_2 \rightleftarrows Ni_2O_3 + 0.5\ O_2,$$

resulting in the formation of a solid solution of nickel dioxide and sesquioxide.

The production of nickel dioxide by dehydrating its hydrate requires extremely long evacuation in vacuum (with a moisture absorbent present) in the cold, at a temperature of zero or below. The dissociation pressure of nickel dioxide is fairly high even at low temperatures, so that dehydrating the hydrate of nickel dioxide must be done by heating it in an autoclave in the presence of phosphoric anhydride under oxygen under pressure that exceeds the dissociation pressure of pure nickel dioxide.

Anhydrous nickel sesquioxide is formed in an atmosphere of air when nickel nitrate is decomposed at 250°. Raising the temperature to 300° initiates the process of dissociation of the nickel sesquioxide, inasmuch as its dissociation pressure becomes higher than the partial pressure of the oxygen in the air. Anhydrous nickel sesquioxide is not very stable at high temperatures, which explains the numerous unsuccessful efforts to prepare it, resulting in a denial of the existence of this compound in the nickel-oxygen system [3].

Chemical analyses of the dissociation products of nickel sesquioxide, produced at various temperatures, did not disclose the presence of the nickel protoxide—sesquioxide. Analysis of the resulting phases of varying composition, as well as X-ray analysis, indicate that solid solutions are formed in the nickel - oxygen system. We must therefore assume that nickel protoxide - sesquioxide is a solid solution of nickel oxides, and not a separate chemical compound. This is also borne out by other physico-chemical research methods. It may therefore be stated that the components of the high-temperature series of solid solutions in the nickel-oxygen system are nickel sesquioxide and protoxide, formed during the decomposition of nickel sesquioxide and its solid solutions with the protoxide in the temperature range of 300-1100°.

Thus, the thermal decomposition of nickel nitrate in air results in the production of nickel sesquioxide or of solid solutions of the nickel sesquioxide and protoxide of varying composition, depending upon the temperature of their formation, or of pure nickel protoxide.

Pure nickel protoxide, as we have said, is bright, light green; it is produced by roasting nickel nitrate in air at temperatures no lower than 1100°. Hence, the numerous methods described in the literature for preparing nickel protoxide by dissociating its nitrate at lower temperatures in the air are wrong. The higher the temperature the closer are the chemical compositions of the solid solutions of nickel oxides that are then formed to that of nickel protoxide.

The change in the composition of solid solutions of nickel sesquioxide and protoxide as a function of the temperature at which they are formed is shown in Fig. 1. As the temperature is raised, the percentage of nickel and of its protoxide in the solid solution gradually increases, while the percentage of oxygen and of the nickel sesquioxide diminishes accordingly, i.e., the composition of solid solutions of nickel oxides in the nickel - oxygen system varies continuously from nickel sesquioxide to nickel protoxide.

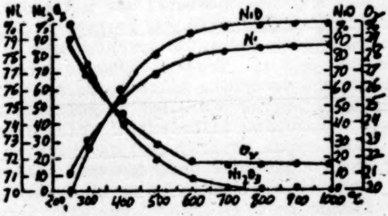

Fig. 1. Composition of solid solutions of nickel oxides as a function of the temperature at which they are produced.

A thermographic study of these problems was made to check the conclusions drawn from the chemical, preparative, and analytical researches. The thermographic investigation of the isobaric process of the thermal dissociation of nickel oxides and of their solid solutions was effected by the method of differential thermal analysis, with automatic recording of the heating and cooling curves on the N.S.Kurnakov recorder.

The dissociation processes of the following compounds were investigated thermographically (in the laboratory of Prof. L.G.Berg, of the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences):

a) Nickel dioxide, produced by dehydrating its hydrate, both by heating under high pressure and in vacuum in the cold with a moisture absorbent present;

b) Oxygen compounds and solid solutions of nickel oxides, produced by dehydrating nickel dioxide, during the heating of the hydrate of nickel dioxide and keeping it at temperatures of 50, 100, and 150° in air until its weight remained constant;

c) Nickel sesquioxide, produced by heating nickel nitrate to a temperature of 250° and heating nickel dioxide to a temperature of 200° and keeping them at those temperatures in air until their weights were constant;

d) Solid solutions of nickel sesquioxide and protoxide, produced by heating nickel dioxide in air to temperatures of 400°, 600°, and other temperatures, until its weight remained constant;

e) Nickel protoxide, produced by roasting nickel sesquioxide at 1150° in an atmosphere of air until its weight remained constant.

The results of thermographic analysis of the isobaric process of thermal dissociation of the oxygen compounds of nickel and of their solid solutions confirm the existence of nickel dioxide, sesquioxide, and protoxide in the nickel - oxygen system, together with solid solutions of the sesquioxide and the protoxide, and of the dioxide and the sesquioxide.

The thermograms indicate that nickel dioxide is the least stable oxygen compound of nickel. Nickel dioxide was observed thermographically to dissociate when heated in air to 70-80°. When heated for a long time, nickel dioxide has been found to dissociate at 50°. Pure nickel dioxide decomposes completely when heated in air to 200-300°, forming the sesquioxide. The dissociation of nickel dioxide from the products of its prolonged heating at lower temperatures is observed to occur at higher temperatures (up to 260°); this is apparently due to a lowering of the dissociation pressure of nickel dioxide, which forms solid solutions with nickel sesquioxide under these conditions. Nickel sesquioxide is found thermographically to begin to decompose in air at 320-330°. When heated for a long time in air until constant weight is reached, it is found to dissociate even at 300°; thus, the temperature conditions for the formation and the stable existence of nickel sesquioxide in pyrometallurgical processes are extremely restricted. In the temperature range of 370-400°, the degree of dissociation of nickel sesquioxide in air is appreciable. The rate of this process drops sharply, however, as the temperature is raised still higher. This is due to the formation of solid solutions of nickel sesquioxide with nickel protoxide, resulting in a lowering of the dissociation pressure of nickel sesquioxide and a reduction of its concentration in the solid solution. That is why the process of dissociation is not always detected at temperatures above 500°, even by the extremely sensitive method of differential thermographic analysis. This is likewise confirmed by the fact that the complete decomposition of nickel sesquioxide takes place only above 1100° under these conditions. The end product is then nickel protoxide. No signs of the formation or existence of nickel protoxide - sesquioxide were found during this process.

Thus, the thermographic analysis of the process of isobaric dissociation of nickel - oxygen compounds shows that - in agreement with the investigation of this problem by other methods - the sole stable oxide of nickel at high temperatures is nickel protoxide, which forms a continuous series of solid solutions with nickel sesquioxide. The concentration of Ni_2O_3 in these solutions is determined by the end temperature of the process of thermal dissociation of nickel sesquioxide or of the solid solutions containing it that are produced at lower temperatures.

In full agreement with these data are the results of the experimental study of the reaction of nickel oxides and of their solid solutions with a 10% solution of H_2SO_4 at 10° and with a 0.1 N solution at 80°. The nickel protoxide enters solution much less than does the sesquioxide. The reaction of solid solutions of nickel protoxide and sesquioxide with solutions of sulfuric acid is characterized by a gradual diminution of the dissolution of nickel as the concentration of the nickel sesquioxide in the solid solutions decreases and that of the nickel protoxide increases (Fig. 2).

The solubility isotherms agree fully with the preceding conclusions regarding the nickel oxides and their solid solutions.

What has been set forth above is likewise confirmed by the data on specific gravity [2], electrical conductivity, and the parameters of the crystal lattices of nickel sesquioxide and protoxide and of their solid solutions (Fig. 3). Magnetometric investigation of the products of the thermal dissociation of nickel dioxide showed that the nickel - oxygen system contained no ferromagnetic compounds. The magnetic properties of "nickel protoxide - sesquioxide" described by Glaser [4] were apparently due to the presence of metallic nickel in the products of the reduction of nickel sesquioxide by hydrogen that he studied.

X-ray analyses (performed in the laboratories of E.S.Makarov and Academician A.A. Bochvar) established that nickel dioxide, produced by dehydrating its hydrate under high pressure, has a cubic lattice with a constant of 4.620 Å. Nickel sesquioxide, produced by dehydrating and decomposing nickel nitrate at 250°, has a face-centered cubic lattice with a parameter of 4.186 A. Nickel protoxide, produced by the thermal dissociation of the higher oxides of nickel at temperatures of 1100 and 1250°, has a somewhat distorted crystal structure of the sodium-chloride type, with a cubic-lattice parameter of 4.172 A, which is subject to further investigation. A study of the structure of nickel sesquioxide and protoxide, as well as of the phases with intermediate compositions, confirms the formation of a series of continuous solid solutions of these oxides. This is borne out by the single type of crystal cubic lattice for all these preparations, by the regular change in the size of the crystal-lattice parameter as the temperature of their production is raised or lowered, and, lastly, by the regular change in the chemical composition of the investigated solid solutions. The appearance of weak interference lines in the X-ray photographs of the oxides whose composition lies in between those of nickel sesquioxide and dioxide, as well as their nature, justify the assumption that nickel dioxide is slightly soluble in nickel sesquioxide in the solid state. Thus, X-Ray analysis not only confirms the existence of nickel dioxide, sesquioxide, and protoxide, but also indicates their structure as well as that of the solid solutions they form.

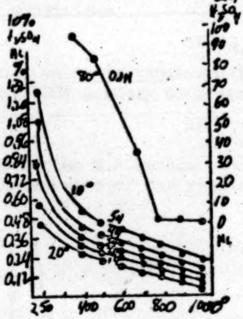

Fig. 2. Reaction of solid solutions of nickel oxides with 10% and 0.1 N solutions of H_2SO_4 at 10 and 80°.

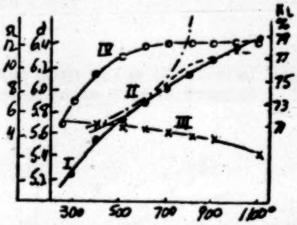

Fig. 3. Variation of the physicochemical characteristics of solid solutions of nickel oxides with their composition and the temperature at which they are produced.

I Specific gravity; II-electrical conductivity, III-crystal lattice parameter, IV-% Ni in the solid solution.

Nor did the X-ray analysis give any indication of the formation of nickel protoxide - sesquioxide. This is also the result arrived at by previously published researches [5-8] on the reduction of the nickel oxides by various methods and, particularly, by the method of differential thermographic analysis.

The experimental data on the equilibrium of the various oxidation-reduction processes in the nickel - oxygen system [2] served as the foundation for our thermodynamic studies. We employed the results of the author's experimental research on the equilibrium of the $NiO + CO \rightleftarrows Ni + CO_2$ reaction [8], the precision and the high reproducibility of which have been repeatedly underscored in domestic and foreign literature [10,11] (Figs. 4, 5), which justifies our concluding that they are quite reliable.

Thermodynamic investigations based on the most accurate and latest data yielded the following: an equation for the temperature variation of the change in enthalpy for the foregoing reaction

$$\Delta H = 12293 - 46000\ T^{-1} - 9.21\ T + 0.0_2492\ T^2 - 0.0_862\ T^3;$$

an equation for the temperature variation of the change in free energy for the same equation

$$\Delta F = 12293 - 23000\ T^{-1} + 21.21\ T \log T - 61.29\ T - 0.0_2492\ T^2 + 0.0_831\ T^3;$$

and equation for the temperature variation of the change in free energy of the formation - dissociation reaction for nickel protoxide

$$\Delta F = \frac{23000}{T} - 27.54\ T \log T + 56.83\ T + 0.0_2772\ T^2 - 0.0_862\ T^3 + 55217;$$

and the heat value of the formation - dissociation reaction for nickel protoxide under standard conditions

$$\Delta H^{o}_{298.1} = -58285\ \text{Cal.}$$

This latter value is close to the result obtained by A.F.Kapustinsky, corresponding member of the USSR Academy of Sciences, and his co-workers [12]:

$$\Delta H^{o}_{298.1} = -58150\ \text{Cal.}$$

Academician M.A.Pavlov [13] gives 58,300 cal as the mean value of several figures for the heat value of the reaction in which nickel protoxide is formed from metallic nickel and oxygen, while Prof. A.N.Volsky [14] takes 58,200 cal as the most probable value of those published in the literature for the heat of formation of nickel protoxide; this agrees with our figure.

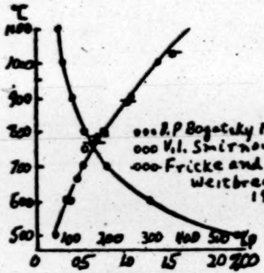

Fig. 4. Variation of the equilibrium of the reaction: $NiO + CO \rightleftarrows Ni + CO_2$ with temperature.

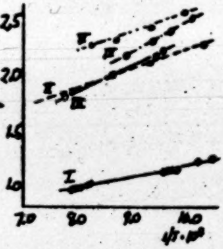

Fig. 5. Reproducibility of the author's experimental data, used as the basis for thermodynamic analyses.

I-$NiAl_2O_4 + CO_2$ $Ni + CO_2 + \gamma \cdot Al_2O_3$ after several measurements; II-$NiO + CO$ $Ni + CO_2$ - Bogatsky; III-$NiO + CO$ $Ni + CO_2$ according to the researches of other authors; IV-$NiO + CO$ $Ni + CO_2$ -Watanabe; V-$NiO + CO$ $Ni + CO_2$-Kapustinsky and Zilberman.

Moreover, we determined the change in the free energy of the formation - dissociation reaction for nickel protoxide under standard conditions:

$$\Delta F^{o}_{298.1} = -52591\ \text{Cal,}$$

and the entropy of nickel protoxide under standard conditions:

$$S^{o}_{298.1} = 8.02\ \text{cal/deg.}$$

Investigation of the equilibrium of the reaction involving the formation - dissociation of nickel protoxide showed that the dissociation pressure of nickel protoxide varies from $1.66\cdot10^{-24}$ atm at 500°C to $1.65\cdot10^{-9}$ atm at 1100° C, which is in good agreement with the corresponding figures obtained by A.F. Kapustinsky and his co-workers [12]. Our researches have shown that the most accurate results are obtained by thermodynamic calculations based on the equation for the variation of the specific heat of nickel protoxide with temperature, obtained calorimetrically by A.F.Kapustinsky [13] and his associates: $\underline{C}_p = 14.1 + 0.31\cdot10^{-3}T - 0.46\cdot\cdot10\,T^{-2}$. The quite satisfactory agreement between the various computed and experimental results shows that this equation is a sufficiently accurate expression for the mean molecular specific heat of nickel protoxide as a function of temperature in the high-temperature ranges.

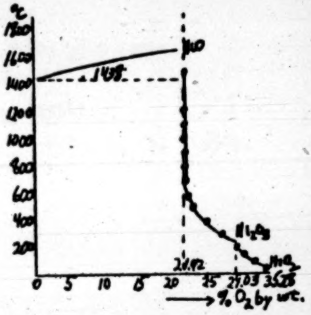

Fig. 6. Temperature-composition diagram of the nickel - oxygen system.

SUMMARY

1. The principal physicochemical properties and the nature of the solid phases in the nickel - oxygen system have been investigated by various analytical methods of physical chemistry.

2. Some of the equilibria in the processes of dissociation, reduction, and oxidation in the nickel-oxygen system have been explored, and thermodynamic computations have been based upon the equilibrium studies.

3. The temperature-composition diagram of the nickel - oxygen system has been plotted from the results of experimental and theoretical investigations.

The foregoing researches have been carried out in consultation with Academicians G.G.Urazov and A.A.Bochvar and with their assistance, and the author wishes to express his profound gratitude to them here.

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THE PRECIPITATION OF HYDROXIDES AS A FUNCTION OF THE SOLUTION pH

I. M. Korenman

The importance of the pH of a solution in the precipitation of metallic hydroxides is discussed in detail in Britton's book [1], which cites considerable experimental data but does not generalize from this data or draw any theoretical conclusions therefrom. A brief discussion of this question, though again without any generalizations, is given in the book by Kolthoff and Sendall [2]. And yet, it is possible to find a mathematical link between the solubility product and the degree of precipitation of the hydroxide, on the one hand, and the solution pH on the other. This is evident from the following equations:

$$Me(OH)_n \rightleftarrows Me^{n+} + n\ OH' \tag{1}$$

$$[Me^{n+}][OH']^n = Sp. \tag{2}$$

Whence:

$$[Me^{n+}] = \frac{Sp}{[OH']^n}. \tag{3}$$

Inasmuch as $[OH'] = \frac{I_{H_2O}}{[H^{\cdot}]}$, Equation (3) may be rewritten as:

$$[Me^{n+}] = \frac{Sp[H^{\cdot}]^n}{I^n_{H_2O}}, \tag{4}$$

where $\underline{n}$ is the valency of the Me cation; $[Me^{n+}]$ is the concentration of Me^{n+} ions in gram-ions per liter; $\underline{S_p}$ is the solubility product of the hydroxide; and I_{H_2O} is the ion product of water.

Taking the logarithms of both sides in Equation (4) and changing signs, we get:

$$pMe^{n+} = npH + pS - npI_{H_2O} \tag{5}$$

or:

$$pH = \frac{pMe^{n+} - pS + npI_{H_2O}}{n} \tag{6}$$

where:

$$pMe^{n+} = -\log\,[Me^{n+}],$$

$$pS = -\log Sp, \qquad pI_{H_2O} = -\log I_{H_2O}.$$

We can use Equation (5) to compute the concentration of Me^{n+} ions in the solution after precipitation as $Me(OH)_n$ at various values of the solution pH. Equation (6) enables us to find the pH at which a given quantity (concentration) of Me^{n+} ions remains in solution after precipitation of the hydroxide. This equation likewise enables us to compute the pH at which the hydroxide begins to precipitate out of a salt solution of known concentration, as well as to compute the pH at which precipitation of the hydroxide practically ceases.

Equation (6) shows that the higher the pMe^{n+} (i.e., the lower the concentration of Me^{n+} ions in the solution), the higher the pH value required for the onset of precipitation and for complete precipitation of the hydroxide. We likewise see that as the pS rises, (i.e., as the solubility product of the hydroxide drops), the pH value for the onset and termination of precipitation diminishes.

In our calculations we must see to it that the maximum solution concentration contains no more than 1 gram-ion per liter (i.e., $pMe^{n+} = 0$) and we must consider precipitation to be complete when the solution contains no more than 10^{-6} gram-ions of Me^{n+} per liter (i.e., $pMe^{n+} = 6$). Substituting these values in Equation (6), we can find the pH for the beginning and end of precipitation of the hydroxide for any practical concentrations of Me^{n+} in the initial solution:

$$\text{Beginning of precipitation:} \quad pH = pI_{H_2O} - \frac{pS}{n}; \qquad (7)$$

$$\text{End of precipitation:} \quad pH = pI_{H_2O} - \frac{pS}{n} + \frac{6}{n}. \qquad (8)$$

All the pH values lying between these extremes may be called the region of hydroxide precipitation.

These formulas enable us to compute that the precipitation of $Fe(OH)_3$ (pS = 37.4) from solutions of ferric-oxide salts of ordinary concentration at room temperature, for example, begins at a pH no lower than 1.6 and ends at a pH no higher than 3.6.

It is more convenient to compare the precipitation regions of different kinds of hydroxides by comparing their solubilities expressed in mols per liter rather than their solubility products or pS. To do this, however, the equations derived above (Table 1) must be transformed by substituting the corresponding solubility values for the pS. The process of computation is illustrated in the following example.

TABLE 1

Region of Hydroxide Precipitation as a Function of the pS at Various Values of n

n	Beginning of precipitation	End of precipitation	Number of pH units in the precipitation region
1	$pH = pI_{H_2O} - pS$	$pH = 6 + pI_{H_2O} - pS$	6
2	$pH = pI_{H_2O} - \frac{pS}{2}$	$pH = 3 + pI_{H_2O} - \frac{pS}{2}$	3
3	$pH = pI_{H_2O} - \frac{pS}{3}$	$pH = 2 + pI_{H_2O} - \frac{pS}{3}$	2
4	$pH = pI_{H_2O} - \frac{pS}{4}$	$pH = 1.5 + pI_{H_2O} - \frac{pS}{4}$	1.5

The onset of precipitation of the hydroxide $Me(OH)_2$ is observed to occur at a pH no lower than

$$pH = pI_{H_2O} - \frac{pS}{2} . \tag{9}$$

The solubility product of the hydroxide is:

$$S_p = [Me^{\cdot\cdot}]\,[OH']^2 = 4[Me^{\cdot\cdot}]^3;$$

whence $\log Sp = 3 \log [Me^{\cdot\cdot}] - \log 4$ or $pS = 3p\,Me^{\cdot\cdot} - 0.6$,
where $[Me^{\cdot\cdot}]$ is the solubility of the hydroxide in mols/liter, or the concentration of $Me^{\cdot\cdot}$ ions in gram-ions/liter in a saturated solution of $Me(OH)_2$.

$$pMe^{\cdot\cdot} = -\log [Me^{\cdot\cdot}].$$

We introduce this value of pS in Equation (9)

$$pH = pI_{H_2O} - \frac{3pMe^{\cdot\cdot} - 0.6}{2} = pI_{H_2O} + 0.3 - 1.5pMe^{\cdot\cdot} . \tag{10}$$

A general equation for these computations may be found by using N.A.Tananayev's formula [3]:

$$[Me^{n+}] = \sqrt[n+1]{\frac{Sp}{n^n}} ; \tag{11}$$

whence:

$$pMe^{n+} = \frac{pS}{n+1} + \frac{\log n^n}{n+1}$$

and

$$pS = (n + 1)\, p\, Me^{n+} - \log n^n. \tag{12}$$

Hence, we get from Equations (7) and (8):

$$pH = pI_{H_2O} - \frac{(n + 1)\, p\, Me^{n+} - \log n^n}{n} \tag{13}$$

for the onset of precipitation, and:

$$pH = pI_{H_2O} + \frac{6}{n} - \frac{(n + 1)\, p\, Me^{n+} - \log n^n}{n} \tag{14}$$

for the end of precipitation.

The figures in Tables 1 and 2 indicate that the region of precipitation of any hydroxide of the $Me(OH)_2$ type includes 3 pH units for any value of pS or pMe^{n+}, the region of precipitation of any hydroxide of the $Me(OH)_3$ type comprises 2 pH units, and so forth. We see that the higher the valency of the cation, the narrower the region of precipitation of the respective hydroxide. It follows that the process of precipitating $Me(OH)_4$ ought to take place more sharply and rapidly, all other conditions being equal, than the precipitation of $Me(OH)_2$ or $MeOH$.

The tables of the pH values at which hydroxides are precipitated, given in various manuals [1,2,4] are of hardly any practical significance. These tables do not indicate whether the pH values refer to the beginning or the end of precipitation, nor do they note the solution concentrations of the initial salts to which these figures apply. The pH values for the precipitation of the same hydroxide are often different in different sources; these discrepancies are due not only to experimental errors, but also to the fact that the figures cited refer to different solution concentrations of the salts before precipitation.

With the equations derived above it is easy to calculate what the molar solubilities or the pMe^{n+} of two hydroxides have to be for one to be able to effect their fractional precipitation by gradually raising the pH, i.e., for the second

TABLE 2

Region of Hydroxide Precipitation as a Function of the pMe^{n+} at Various Values of n

n	Beginning of precipitation	End of precipitation	Number of pH units in the precipitation region
1	$pH = pI_{H_2O} - 2pMe^{\cdot}$	$pH = pI_{H_2O} + 6 - 2pMe^{\cdot}$	6
2	$pH = pI_{H_2O} + 0.3 - 1.5pMe^{\cdot\cdot}$	$ph = pI_{H_2O} + 3.3 - 1.5pMe^{\cdot\cdot}$	3
3	$pH = pI_{H_2O} + 0.47 - 1.33pMe^{\cdot\cdot\cdot}$	$pH = pI_{H_2O} + 2.47 - 1.33pMe^{\cdot\cdot\cdot}$	2
4	$pH = pI_{H_2O} + 0.6 - 1.25pMe^{\cdot\cdot\cdot\cdot}$	$pH = pI_{H_2O} + 2.1 - 1.25pMe^{\cdot\cdot\cdot\cdot}$	1.5

hydroxide to start precipitating only after practically all the first one has been thrown down.

Let us begin by considering the fractional precipitation of two hydroxides of the $Me(OH)_2$ type. At some pH for the solution, all of $Me_I(OH)_2$ will be thrown down while the $Me_{II}(OH)_2$ is just beginning to precipitate. When this is the case, the following equation applies:

$$pI_{H_2O} + 3.3 - 1.5pMe_I^{\cdot\cdot} = pI_{H_2O} + 0.3 - 1.5\,pMe_{II}^{\cdot\cdot},$$

whence:

$$1.5pMe_I^{\cdot\cdot} - 1.5\,pMe_{II}^{\cdot\cdot} = 3 \text{ or } pMe_I^{\cdot\cdot} - pMe_{II}^{\cdot\cdot} = 2$$

This means that the feasibility of the fractional precipitation of two hydroxides of the $Me(OH)_2$ type requires that their $pMe^{\cdot\cdot}$ differ by at least 2 unites, i.e., that the solubility of one of them be at least 100 times less than that of the other.

The fractional precipitation of $Me(OH)_2$ and $Me(OH)_3$ involves two possible cases:

a) $pMe^{\cdot\cdot} > pMe^{\cdot\cdot\cdot}$ – $Me(OH)_2$ precipitates first;

hence:

$$pI_{H_2O} + 3.3 - 1.5pMe^{\cdot\cdot} = pI_{H_2O} + 0.47 - 1.33\,pMe^{\cdot\cdot\cdot};$$

whence:

$$1.5pMe^{\cdot\cdot} - 1.33pMe^{\cdot\cdot\cdot} = 2.8 \text{ or } pMe^{\cdot\cdot} - pMe^{\cdot\cdot\cdot} \simeq 2.$$

b) $pMe^{\cdot\cdot} < pMe^{\cdot\cdot\cdot}$ – $Me(OH)_3$ precipitates first, and therefore the following equation holds for the instant when the precipitation of $Me(OH)_3$ is complete and the precipitation of $Me(OH)_2$ is setting in:

$$pI_{H_2O} + 2.47 - 1.33pMe^{\cdot\cdot\cdot} = pI_{H_2O} + 0.3 - 1.5\,pMe^{\cdot\cdot};$$

whence:

$$1.33pMe^{\cdot\cdot\cdot} - 1.5pMe^{\cdot\cdot} = 2.17, \text{ or } pMe^{\cdot\cdot\cdot} - pMe^{\cdot\cdot} \simeq 1.5.$$

The problems involved in the fractional precipitation of other pairs of hydroxides may be solved in a similar fashion.

In their general form, this function may be expressed as follows, bearing in mind that the pH at the end of precipitation of the first hydroxide (Equation 14) must be equal to (or less than) the pH at the beginning of precipitation of the second hydroxide (Equation 13):

$$pI_{H_2O} + \frac{6}{n_1} - \frac{(n_1 + 1)Me_I - \log n_1^{n_1}}{n_1} \leqslant pI_{H_2O} - \frac{(n_2+1)pMe_I - \log n_2^{n_2}}{n_2};$$

whence

$$\frac{(n_1 + 1)pMe_I - \log n_1^{n_1}}{n_1} - \frac{(n_2 + 1)pMe_{II} - \log n_2^{n_2}}{n_2} \geqslant \frac{6}{n_1}. \qquad (15)$$

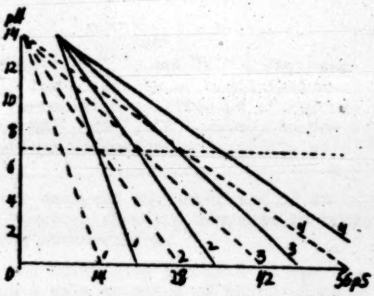
This equation becomes much simpler when we use the values of pS (Equations 8 and 7):

$$pI_{H_2O} + \frac{6}{n_1} - \frac{pS_1}{n_1} \leqslant pI_{H_2O} - \frac{pS_2}{n_2};$$

whence

$$PS_1 - \frac{n_1}{n_2} pS_2 \geqslant 6. \qquad (16)$$

The figure shows the pH of the beginning and end of precipitation of a hydroxide from 1N or more dilute solutions of Me^{n+} as a function of n and pS. The figure, together with the data listed in the tables, enables us to draw the following conclusions:



The pH at the beginning and end of precipitation of a hydroxide: Broken lines – beginning of precipitation; solid lines – end of precipitation.

1-MeOH hydroxides; 2-Me(OH)$_2$ hydroxides; 3-Me(OH)$_3$ hydroxides; 4-Me(OH)$_4$ hydroxides.

a) At identical values of pS or pMe^{n+} and with all the other conditions equal, the onset of precipitation occurs at pH values whose magnitude rises with the valency of the cation;

b) The onset of precipitation of relatively easily soluble hydroxides takes place only in strongly alkaline media, while the precipitation of hydroxides that dissolve with great difficulty begins in acid media;

c) Since the maximum pH value attainable in practice does not exceed 14, it may be computed that complete precipitation is achieved only for hydroxides whose pS is no lower than 6, no matter what the valency of the cation;

d) Since the minimum pH value practically attainable is not below zero, it is easy to prove by calculation that cations whose pS is higher than 14n cannot produce even highly acidulated salt solutions. In actuality, the pS of hydroxides produced by precipitation from their respective salts does not exceed these values. The sole exception is $Tl(OH)_3$, the pS of which is 52.85 [5] instead of the maximum value of 42 for hydroxides of this type;

e) When pS > 7n, the hydroxide begins to precipitate out of acid solutions;

when $pS < 7n$ precipitation sets in only in alkaline media. We may conclude from this that salts of strong acids and hydroxides that begin to precipitate from acid media form aqueous solutions with acid reactions. On the other hand, salts of strong acids and hydroxides that are precipitated from alkaline media form slightly acid or neutral aqueous solutions. This means that the higher the pH at which precipitation of the hydroxide sets in, the stronger a base will it be.

By way of example we have listed hydroxides of the alkaline-earth metals in Table 3.

TABLE 3

Hydroxide	Solubility mols/liter [5]	pH at which precipitation begins	Strength of base
$Be(OH)_2$	$8 \cdot 10^{-8}$	~ 6.5	Weak base
$Mg(OH)_2$	$1.1 \cdot 10^{-4}$	~ 11	↓
$Ca(OH)_2$	$2 \cdot 10^{-2}$	> 12	
$Sr(OH)_2$	$6.7 \cdot 10^{-2}$	Does not precipitate	
$Ba(OH)_2$	$2.2 \cdot 10^{-1}$	ditto	Strong base

B.V.Nekrasov [6] has pointed out the parallelism between the solubility of the hydroxides of the alkaline-earth metals and their basic properties: the stronger bases are more soluble in water. Here we note the relationship between these properties and the pH at which precipitation sets in. It is not only in the series of related elements that this sort of parallelism exists. The aqueous solutions of the chlorides of $Sn^{\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$, and $Fe^{\cdot\cdot\cdot}$, for example, are strongly acid, testifying to the extremely low constants of basic ionization of the respective hydroxides; the latter are formed at a solution pH of approximately 2-3. The aqueous solutions of chlorides of $Cd^{\cdot\cdot}$ $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, etc., on the other hand, are practically neutral, and the respective hydroxides precipitate at $pH > 7$.

Thus, the lower the solubility, the weaker the base and the lower the pH at which precipitation sets in. This does not mean, however, that the converse is true, inasmuch as not all readily soluble bases are strong electrolytes.

Equations (5) or (4) may be used to compute the solubility products of hydroxides when the pH at which precipitation begins from a salt solution of given concentration is known:

$$pS = pMe^{n+} - n\,pH + npI_{H_2O}. \qquad (17)$$

$$Sp = \frac{[Me^{n+}]I^{n}_{H_2O}}{[H^{\cdot}]^{n}}. \qquad (18)$$

We have carried out a series of such computations, based upon the pH values at which the precipitation of several hydroxides sets in [1,2] (Tables 4 and 5).

Our results show that calculating the solubility product of a hydroxide from the pH at which it begins to precipitate out of a salt solution of known concentration yields figures in some instances that are in good agreement with the values found by other methods. It should be noted, however, that in some instances computation yielded unsatisfactory results as in the calculations for $Cu(OH)_2$ and $Cd(OH)_2$, which may be due to inaccurate determination of the pH at which the hydroxide begins to precipitate. In any event, the order of magnitude of the solubility products is nearly always the same as the order of magnitude for these quantities found by other methods.

TABLE 4

Salt	Salt concentration, mols/liter	pH at which the hydroxide begins to precipitate (at 18°)
$MnCl_2$	0.024	8.41
$CoCl_2$	0.025	6.81
$NiCl_2$	0.025	6.66
$FeSO_4$	0.025	5.49
$ZnSO_4$	0.025	5.20
$ZnSO_4$	0.25	5.8
$ZnSO_4$	0.01	6.5
$Cr_2(SO_4)_3$	0.005	5.34
$FeCl_3$	0.0133	2.3

TABLE 5

Solubility Products of Hydroxides, Computed from Equations (11) and (12)

Salt	Hydroxide solubility product	
	Computed	Literature data
$MnCl_2$	$8\cdot10^{-11}$	$4\cdot10^{-14}$ [7]
$CoCl_2$	$5\cdot10^{-17}$	$1.6\cdot10^{-18}$ [5]
$NiCl_2$	$4\cdot10^{-17}$	$8.7\cdot10^{-19}$ [5]
$FeSO_4$	$1.2\cdot10^{-19}$	$4.5\cdot10^{-21}$ [5]
$ZnSO_4$	$3.1\cdot10^{-20}$	$1\cdot10^{-17}$ [7]
$ZnSO_4$	$5\cdot10^{-18}$	$1\cdot10^{-17}$ [7]
$ZnSO_4$	$6.3\cdot10^{-18}$	$1\cdot10^{-17}$ [7]
$Cr_2(SO_4)_3$	$4\cdot10^{-29}$	$5.4\cdot10^{-31}$ [5]
$FeCl_3$	$3.1\cdot10^{-38}$	$3.8\cdot10^{-38}$ [7]

The figures in Tables 4 and 5 allow us to conclude that the method of determining the solubility products of hydroxides from the pH value at which their precipitation sets in yields results that are satisfactory.

Similar statements may be made with regard to the variation of precipitation of difficultly soluble acids with the [illegible]f the solution. This will be the subject of a separate report.

Lastly, the equations derived above make possible a critical appraisal of the values of the solubility products of some hydroxides. We are referring to $Al(OH)_3$, the solubility product of which, cited in several manuals, cannot explain the behavior of $Al(OH)_3$ in some processes. Two values are cited for the solubility product of this hydroxide: $1.1\cdot10^{-15}$ [7] and $4.7\cdot10^{-18}$ [5], the respective solubilities in water being $7.9\cdot10^{-5}$ mols/liter and $2\cdot10^{-5}$ mols/liter. This means that the concentration of OH' ions in a saturated solution of $Al(OH)_3$ is $2.4\cdot10^{-4} - 6\ 10^{-5}$ gram-ions/liter. Precipitating the hydroxide from a solution of an aluminum salt requires a higher concentration of OH' ions than exists in a saturated $Al(OH)_3$ solution. The concentration of OH' ions in a 0.1 solution of NH_4OH, containing 1 mol of NH_4Cl per liter is $2.5\cdot10^{-6}$ gram-ions/ liter*, i.e., considerably less than is required for the precipitation of $Al(OH)_3$ and according to this calculation, but contrary to the facts, such a solution of ammonia ought not to precipitate $Al(OH)_3$. If we increase the NH_4OH concentration to 1 mol/liter or reduce the concentration of NH_4Cl to 0.1 mol/liter, the concentration of OH' ions will be inadequate for the precipitation of $Al(OH)_3$, if we assume that the latter's solubility product is really 10^{-15} or 10^{-18}. Experiment shows, however that $Al(OH)_3$ is precipitated at a concentration of OH' ions that is less than 10^{-6} gram-ions per liter. Hence, the concentration of OH' ions in a saturated solution of $Al(OH)_3$ must be much lower than 10^{-6} gram-ions per liter, and $\underline{Sp} < 10^{-18}$.

Now let us consider this problem from another angle. We know that $Al(OH)_3$ can be precipitated without precipitating $Mg(OH)_2$ by using a solution of ammonia and ammonium chloride.

According to Equation (16), this precipitation requires that:

$$pS_{Al(OH)_3} - \frac{3}{2}\,pS_{Mg(OH)_2} \geqslant 6. \qquad (19)$$

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*Cf V.I. Petrashen [9] and H Britton [10] for this calculation

The pS values for these hydroxides derived from the data cited above ($pS_{Al(OH)_3} = 16.96$ or 19.33; $pS_{Mg(OH)_2} = 12.92$) indicate that $Al(OH)_3$ cannot be fractionally precipitated, inasmuch as the difference in Equation (19) is much less than 6. But this conclusion contradicts the well-known facts and merely indicates that the values cited in the literature for the solubility product of $Al(OH)_3$ are inaccurate. Fractional separation of $Al(OH)_3$ requires that

$$pS_{Al(OH)_3} > 6 + \frac{3}{2}\, pS_{Mg(OH)_2},$$

i.e., the solubility product of $Al(OH)_3$ must be no higher than 10^{-26} ($pS > 26$).

If the pS of aluminum hydroxide actually equaled 18, its precipitation ought to set in at a pH of 8 or more, according to Equation (7), which is likewise contradicted by the fact that $Al(OH)_3$ begins to precipitate at a pH of 4 – 5 [1,2]. This indicates that the pS of aluminum hydroxide must be of the order of 10^{-30}.

The solubility product of Al(OH) may be computed by means of Equation (17) from the figures cited by Britton [10] for the pH at which an alkali causes precipitation to set in from solutions of $Al_2(SO_4)_3$ and $AlCl_3$.

TABLE 6

Solubility Product of $Al(OH)_3$ t=18°

Aluminum salt	Salt concentration, mols/liter	pH at which precipitation begins	pS $Al(OH)_3$	Sp $Al(OH)_3$
Sulfate	0.00667	4.14	31.86	$1.4\cdot10^{-32}$
Sulfate	0.00349	4.14	32.14	$7.2\cdot10^{-33}$
Chloride	0.00333	4.76	30.62	$2.4\cdot10^{-31}$
Chloride	0.00408	4.69	30.74	$1.8\cdot10^{-31}$

The last two figures must be considered less accurate, inasmuch as the tendency of $Al(OH)_3$ to form colloidal solutions in the presence of chlorides causes the observation of the precipitate by the naked eye to lag behind the onset of $Al(OH)_3$ precipitation.

The foregoing data justify the assertion that the solubility product of $Al(OH)_3$ is 10^{-32}. This value agrees with the actual behavior of $Al(OH)_3$.

SUMMARY

1. Equations have been derived for computing the pH at which the precipitation of hydroxides begins and ends.

2. The conditions for the fractional precipitation of hydroxides have been established.

3. It has been shown that the solubility product of a hydroxide can be calculated from the pH at which it begins to precipitate.

4. It has been shown that the solubility product of aluminum hydroxide must be of the order of magnitude of 10^{-32}.

5. It has been shown that the solubility product, the pH at which a hydroxide begins to precipitate, and its strength as a base are all interrelated.

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COMPLEX FLUORIDES OF BERYLLIUM IN SOLUTION

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Several fluoride compounds of beryllium of the $MeBeF_3$, Me_2BeF_4, and $Me'BeF_4$ type and composite compounds of the $Me_2BeF_4 \cdot Me'BeF_4 \cdot 6H_2O$ type, in which Me is an alkali (or an ion of ammonia), and Me' is a bivalent metal, such as strontium, cobalt, zinc, iron (II), and the like, are known [1]. I.V.Tananayev and E.N.Deitchman have shown that the solution may contain, not only the complex ions BeF_4^{--} and BeF_3^{--} and the electroneutral molecules BeF_2, but also – under certain conditions – complex ions with a single addendum: BeF^+ [2].

The experimental proof of the existence of complex beryllium-monofluoride ions in solutions was not unexpected, inasmuch as step-by-step dissociation in a solution has been shown to exist for many salts, including several fluorides.

Thus, several coordination forms have been demonstrated for aluminum and iron (III) with fluorides in aqueous solution [2,3,4].

Inasmuch as the properties of solutions of aluminum and beryllium salts – especially their fluoride compounds – are very much alike, we might have expected that there are complex monofluoride ions of beryllium, as had been previously found to be the case for aluminum.

We also know that the strength of the bond to fluorine in aluminum and beryllium compounds is high enough to prevent the precipitation of fluorine ions from the solution (say, by calcium ions). Yet the literature contains no quantitative information on the stability of solutions of beryllium-fluorine coordination compounds.

In a fairly recent paper, V.M.Tarayan has shown that the concentration of beryllium in a solution containing magnesium ions may be determined by means of potentiometric titration with a sodium fluoride solution [5]. Unfortunately, it is impossible to titrate aluminum and beryllium separately when aluminum ions are present, since there is no potential jump between the end of the aluminum titration and the beginning of the beryllium titration, the curve exhibiting a sharp bend only after all the aluminum and beryllium ions have been bound in complex fluorides.

Not only does this indicate that the dissociation constants for aluminum and beryllium fluorides are close together, but it also shows that aluminum-fluorine coordination compounds are only slightly more stable than the beryllium ones. In their paper mentioned above, I.V.Tananayev and E.N.Deitchman investigated the variation of the hydrogen-ion concentration with the concentration of hydrofluoric acid and the beryllium salt by measuring the e.m.f.'s in the $BeF_2 - HF - H_2O$ and $BeCl_2 - HF - H_2O$ systems.

But we were unable to compute the stability of complex beryllium-fluorine ions in solution from this paper either.

The present research was undertaken in order to fill this gap.*

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*After this paper had been written, a new report by I V Tananayev and E N Deitchman appeared. In a study of the solubilities of CaF_2, LiF and PbFCl in solutions of $Be(NO_3)_2$ these authors obtained divergent values for the dissociation constant of BeF^+ [14] (cf footnote on p 23, this text.)

EXPERIMENTAL

Method. We determined the stability of complex beryllium-fluorine ions by using a method we had employed earlier to determine the value of the dissociation constant of iron (III) and of complex aluminum-fluorine ions in solution [3,4].

In this method we estimated the formation of coordination compounds between ions of one metal or another and fluorine ions, as well as the stability of the bonds within the complex ions, from the change in the concentration of the colored ferrithiocyanate ions. This calculation of the stability of complex ions was based upon the fact that the equilibrium in the

$$Fe(NO_3)_3 - KSCN - NaF - Be(NO_3)_2$$

system in an aqueous nitric-acid solution depends upon the concentration of the components and the ratios of the values of the dissociation constants of the complex ions formed within the system. Since the values of the dissociation constants of HF and of the complex ions $Fe(SCN)^{++}$ and FeF^{++} are known [3,4,6], while the salt concentrations can be chosen arbitrarily, we are able to determine the value of the dissociation constant of complex beryllium-monofluoride ions. But computing the equilibrium concentrations of the components entering into the expression:

$$K_{BeF^+} = \frac{[Be^{++}][F^-]}{[BeF^+]},$$

requires the performance of a series of calculations, since only one quantity – the concentration of $Fe(SCN)^{++}$ – can be determined experimentally under our conditions.

The concentration of $Fe(SCN)^{++}$ was determined by measuring and comparing the optical density of two solutions in a photocolorimeter, using a diaphragm and a green light filter for compensation.

Our previous paper [4] should be consulted for details of this method and the calculations involved.

Materials. The ferric nitrate and potassium thiocyanate were recrystallized, the sodium fluoride was freed of its traces of silicon fluoride by using potassium chloride and then evaporating the solution [7], and the nitric acid was redistilled. Solutions of these salts in 0.1N nitric acid were prepared and standardized as described previously [3].

In preparing a solution of beryllium nitrate, we started out with an anhydrous preparation of beryllium hydroxide which was purified as follows. After the beryllium hydroxide had been twice precipitated with ammonia solution*, the carefully washed hydroxide precipitate was treated with a solution of ammonium carbonate; after it had dissolved completely, a freshly prepared solution of ammonium sulfide was added. The precipitated sulfides were filtered out of the solution, which was then set aside to stand overnight. After having been heated over a water bath, the newly formed sulfides were again filtered out of the solution, and the ammonium carbonate present in excess in the solution was decomposed with a strong current of steam [8].

The beryllium carbonate that was recovered was separated from the solution and washed. It was snow white, and a sample prepared by dissolving some of it in hydrochloric acid was colorless.

Then the hydroxide was precipitated with ammonia from a solution of this preparation in nitric acid; after having been washed with an abundant quantity of hot water, the precipitate was treated with 0.2N nitric acid. Not enough nitric acid was used to dissolve all the hydroxide. The day after the nitric-acid treatment the undissolved portion of the precipitate was filtered out of the solution. The concentration of beryllium in the solution was determined gravimetrically as BeO [9]. In our research, we used a solution that was 0.01 molar with respect to beryllium and 0.1N with respect to HNO_3.

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*First from a hydrochloric acid solution and then from a nitric acid solution.

Dissociation Constant of Complex BeF^+ Ions

As we have pointed out, the whole experiment made to determine the value of the dissociation constant of the complex BeF^+ ions boiled down to a determination of the concentration of the $Fe(SCN)^{++}$ in the presence of $Be(NO_3)_2$ and NaF. This determination was made in every individual case by comparing the optical density of solutions containing $Fe(NO_3)_3$, KSCN, $Be(NO_3)_2$, and NaF (the solutions under test), with the optical density of solutions containing nothing but $Fe(NO_3)_3$, KSCN, and $Be(NO_3)_2$ (the comparison solutions). The concentration of HNO_3 was 0.1N in all the solutions.

We first determined that the complex BeF^+ ions are formed at a NaF concentration of the order of 10^{-4} mol per liter. This is illustrated by the curve in Fig. 1, which was plotted, as outlined by Job [10], for an aggregate concentration of $4 \cdot 10^{-4}$ mol per liter for $Be(NO_3)_2$ and NaF. We shall not cite other experimental data here, inasmuch as they are similar to those obtained in the determination of the composition of complex aluminum fluorine ions under analogous conditions [4]. In our determination of the value of the dissociation constant for BeF+ the concentration of ferric nitrate was $20 \cdot 10^{-5}$ mol/liter in all the solutions (test and comparison solutions), while that of the KSCN was $199.2 \cdot 10^{-5}$ mol/liter. The concentrations of beryllium nitrate and sodium fluoride varied· they are given in Table 1.

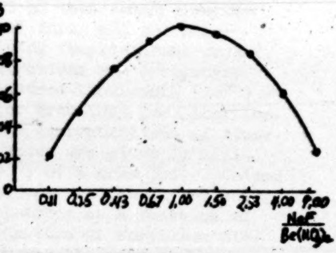

Fig. 1

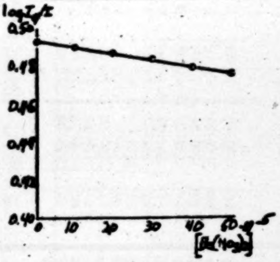

Fig. 2.

During our measurement of the optical density of the solutions we found that the intensity of the color of the ferrithiocyanate solution (without the NaF) is somewhat diminished by beryllium nitrate. This action of the beryllium salt upon nitric acid (0.1 N HNO_3) solutions containing the above-mentioned concentrations of iron (III) nitrate and potassium thiocyanate is illustrated in Fig. 2. The concentrations of $Be(NO_3)_2$ are plotted along the axis of abscissas in mols per liter, with the optical density ($\log I_0/I$) plotted along the axis of ordinates. When the concentration of beryllium nitrate is $50 \cdot 10^{-5}$ mol/liter, the color intensity of the solution is diminished about 3.5%. The color is found to grow equally weaker when the beryllium nitrate in the ferrithiocyanate solution is replaced by enough sodium nitrate to ensure that the ionicity of both solutions is the same. We may therefore conclude that the color is weakened as the result of physical rather than chemical causes. And if we assume that some chemical action does take place nonetheless, it must be extremely insignificant and its products must be quite unstable.

To eliminate this action of the beryllium nitrate, the comparison solutions contained the same concentrations of beryllium nitrate as the test solutions, in addition to the ferric nitrate and the potassium thiocyanate.

The experimental and computational results are listed in Table 1. Columns 2-5 of this table give the experimental data; all the other columns giving computational values. The concentrations are everywhere given in hundred-thousandth (10^{-5}) of a mol (or gram-ion) per liter [except for the concentrations of fluorine ions, which are given in millionths (10^{-6}) of a gram ion]. Column 2 gives the optical density of comparison solutions as a function of the concentration of beryllium nitrate, which was the same in the comparison and the test solutions and is listed in Column 3. Column 4 gives the concentration of sodium fluoride in the test solutions; while Column 5 gives the optical density of these solutions. The concentration of $Fe(SCN)^{++}$ (Column 7) was always found by multiplying the figures in Column 6 (the ratio of the optical densities of the test and comparison solutions) by $6.55 \cdot 10^{-5}$. The latter figure is the concentrations of $Fe(SCN)^{++}$ in the comparison solutions (in mols/liter) for the concentrations of ferric nitrate and potassium thiocyanate specified above ($20.16 \cdot 10^{-5}$ and $199.2 \cdot 10^{-5}$ mols/liter),

TABLE 1

$[Fe(NO_3)_3] = 20.16 \cdot 10^{-5}$; $[KSCN] = 199.2 \cdot 10^{-5}$; $[HNO_3] = 0.1$ mol/liter.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
No.	$\log \frac{I_0}{I}$ comparison solution	$[Be(NO_3)_2]$	$[NaF]$	$\log \frac{I_0}{I}$ test solutions	$\log \frac{I_0}{I_{test}}$ / $\log \frac{I_0}{I_{comp}}$	$[Fe(SCN)^{++}]$	$[(SCN)^-]$	$[Fe^{+++}]$	$[FeF^{++}]$	$[F^-]$	$[HF]$	$[HF]+[F^-]+[FeF^{++}]$	$[BeF^+]$	$[Be^{++}]$	K_{BeF^+}
1		20	10	0.4616	0.9498	6.22	192.98	12.89	1.05	0.407	4.07	5.18	4.84	15.16	1.28
2		20	20	0.4330	0.8909	5.84	193.36	12.08	2.24	0.93	9.26	11.59	8.41	11.59	1.28
3		20	30	0.4044	0.8321	5.45	193.75	11.25	3.46	1.54	15.4	19.01	10.99	9.01	1.26
4	0.4860	20	40	0.3766	0.7749	5.07	194.13	10.45	4.64	2.22	22.1	26.96	13.04	6.96	1.19
5		20	50	0.3489	0.7179	4.70	194.5	9.67	5.79	2.99	29.8	35.89	14.11	5.89	1.25
6		30	20	0.4413	0.9140	5.99	193.21	12.4	1.77	0.71	7.09	8.93	11.07	18.93	1.21
7		30	30	0.4151	0.8598	5.63	193.57	11.63	2.90	1.25	12.48	15.51	14.49	15.51	1.34
8		30	40	0.3915	0.8109	5.31	193.89	10.95	3.90	1.78	17.77	21.85	18.15	11.85	1.16
9		40	10	0.4608	0.9612	6.29	192.91	13.04	0.83	0.32	3.2	4.06	5.94	34.06	1.83
10	0.4794	40	20	0.4437	0.9255	6.06	193.14	12.56	1.54	0.613	6.13	7.73	12.27	27.73	1.39
11		40	30	0.4293	0.8955	5.86	193.34	12.12	2.18	0.[illegible]	9.02	11.26	18.74	21.26	1.03
12	0.4763	50	20	0.4461	0.9366	6.13	193.07	12.70	1.23	0.52	5.2	6.58	13.42	36.58	1.42

with no beryllium nitrate present.*

Inasmuch as the above-mentioned influence of $Be(NO_3)_2$ upon the optical density of the solutions was eliminated by having it present in equal concentrations in the test solutions and in the comparison solutions, this figure may be taken for our subsequent calculations.

The last column of Table 1 gives the computed values of the dissociation constant of complex beryllium-monofluoride ions.

The mean value of the $\underline{K}_{BeF^+}$ is $1.3 \cdot 10^{-6}$.** It was previously determined that the values of the dissociation constants for FeF^{++} and AlF^{++} are $5 \cdot 10^{-6}$ and $5 \cdot 10^{-7}$, respectively [3,4]. Thus, the stability in solution of the coordination compounds of iron (III), beryllium, and aluminum with fluorine differ but slightly, with the coordination compound of beryllium with fluorine lying in the middle.

This explains the impossibility of potentiometrically titrating aluminum and beryllium separately with sodium fluoride when they are present together [5]; it also enables us to predict that such titration cannot be effected when the ions of iron (III) and beryllium are present together. It may be supposed that when the ions of iron (III), beryllium, and aluminum are all present in a solution together, it will likewise be impossible to determine them separately by potentiometric titration with sodium fluoride, since the beryllium ions smooth out the potential jump between the end of the aluminum titration andthe beginning of the iron titration.

Nor is it likely that the concentration of beryllium in a solution can be determined by titration with sodium fluoride in the presence of ferric thiocyanate as an indicator.

Coordination Compounds of Fluorine and Beryllium With a Large Number of Coordinated Fluorine Ions

As we have pointed out at the beginning of this paper, it is a matter of common knowledge that a solution may contain complex ions of beryllium fluoride with addenda ranging from 1 to 4 in number, i.e., up to the maximum coordination number possible for beryllium.

It is apparent that these complex ions are formed step by step, and that the concentration of one complex group or another depends upon the concentration of the fluorine ions to be coordinated as well as upon the stability of the complex groups. The stability of the complex groups, i.e., the values of the dissociation constants, may be calculated, as we have done previously [3,4], by making use of the linkage coefficients between $\underline{pK}$ derived by A.K.Babko [11,12] (= - log K),

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* The concentration of $Fe(SCN)^{++}$ in the comparison solutions may be readily computed from the equation:

$$K_{Fe(SCN)^{++}} = \frac{([Fe(NO_3)_3] - x)([KSCN] - x)}{x} = 4 \cdot 10^{-3}$$

where x is the concentration of $Fe(SCN)^{++}$. At $[Fe(NO_3)_3] = 20.16 \cdot 10^{-5}$ and $[KSCN] = 199.2 \cdot 10^{-5}$ mol per liter, $x = 6.55 \cdot 10^{-5}$ mol per liter.

** According to I.V.Tananayev and E.N.Deitchman, the mean value of the dissociation constant of BeF^+, found in a study of solubility of CaF_2, LiF and PbFCl in $Be(NO_3)_3$ solutions is $6.4 \cdot 10^{-5}$, computed from tests with CaF_2 (4 experiments), and $5.1 \cdot 10^{-5}$ computed from tests with PbFCl (5 experiments) [14]. The first figure is fairly close to the value we have found. It should be noted that the authors themselves consider their figures approximations, owing to certain assumptions they made in the course of their computations.

The values of the step-by-step dissociation constants of complex ions of beryllium and fluorine, computed in this way, are as follows:

$$K_{BeF_2} = \frac{[BeF^+][F^-]}{[BeF_2]} = 1.14\cdot10^{-5}; \qquad K_{BeF_3^-} = \frac{[BeF_2][F^-]}{[BeF_3^-]} = 2.75\cdot10^{-4};$$

$$K_{BeF_4^{--}} = \frac{[BeF_3^-][F^-]}{[BeF_4^{--}]} = 1.02\cdot10^{-2}.$$

If we assume that the dissociation of BeF_4^{--} complex ion takes place as follows: $BeF_4^{--} \rightleftarrows Be^{++} + 4F^-$, the aggregate equilibrium constant will be

$$K = \frac{[Be^{++}][F^-]^4}{[BeF_4^{--}]} = K_{BeF^+}\cdot K_{BeF_2}\cdot K_{BeF_3^-}\cdot K_{BeF_4^{--}} = 4.16\cdot10^{-17}.$$

The values of the step-by-step dissociation constants may be used to obtain an idea – by means of computation – of the relationships between the concentrations of the complex ions for various concentrations of fluorine in the solution.

If we take the gross concentration of beryllium in the solution as equaling 100, then

$$100 = [Be^{++}] + [BeF^+] + [BeF_2] + [BeF_3^-] + [BeF_4^{--}].$$

This expression can be rewritten as:

$$100 = [Be^{++}] + [Be^{++}]\frac{[F^-]}{K_{BeF^+}} + [Be^{++}]\frac{[F^-]^2}{K_{BeF^+}\cdot K_{BeF_2}} +$$

$$+ [Be^{++}]\frac{[F^-]^3}{K_{BeF^+}\cdot K_{BeF_2}\cdot K_{BeF_3^-}} + [Be^{++}]\frac{[F^-]^4}{K_{BeF^+}\cdot K_{BeF_2}\cdot K_{BeF_3^-}\cdot K_{BeF_4^{--}}}$$

and

$$[Be^{++}] = \frac{100}{1 + \frac{[F^-]}{K_1} + \frac{[F^-]^2}{K_1\cdot K_2} + \frac{[F^-]^3}{K_1\cdot K_2\cdot K_3} + \frac{[F^-]^4}{K_1\cdot K_2\cdot K_3\cdot K_4}}$$

The latter equation may be solved for a series of concentrations of fluorine ions, the $[Be^{++}]$ being expressed in per cent.

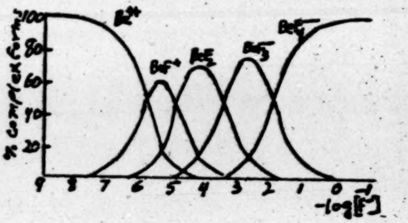

Fig. 3.

The product of $[Be^{++}]$ and the calculated coefficients

$$\frac{[F^-]}{K_1}, \ldots \frac{[F^-]^4}{K_1\cdot K_2\cdot K_3\cdot K_4}$$

gives the concentration (in %) of the corresponding complex groups for the given concentrations of fluorine ions.

The computational results for concentrations of fluorine ions ranging from $1\cdot10^{-9}$ to 10 gram-ions per liter are represented in the form of a diagram in Fig. 3. The negative logarithm of the concentration of fluorine ions ($-\log[F^-]$), is plotted along the axis of abscissas, and the per cent concentration of the complex forms along the axis of ordinates.

One of the conclusions that may be drawn from an inspection of this diagram is that it is generally difficult to produce acid solutions containing nothing but BeF_4^{--} ions (unless solutions of hydrofluoric acid are used). For nearly all of the beryllium to be present as BeF_4^{--} ions, the concentrations of fluorine ions in the solution must be of the order of one gram-ion per liter, as the diagram indicates. But inasmuch as the concentration of fluorine ions is an insignificant part of the fluoride concentration in acid solutions (of the order of 0.01), the concentration of the fluoride must be incommensurably high. That is why sodium fluoride may prove to be unsuitable for this purpose owing to its limited solubility. The conditions for the formation of BeF_4^{--} ions are more favorable in neutral or alkaline solutions.

Complex Fluorides of Beryllium in Alkaline Solutions

Calculating the stability of complex fluorides of beryllium in alkaline solutions is a topic of some interest.

The solubility product (L_p) of beryllium hydroxide is $2.1 \cdot 10^{-15}$ at 18° for dissociation of the alkali type [13].

The values of the equilibrium constant of the:

$$BeF_n^{(2-n)} + 2OH^- \rightleftarrows Be(OH)_2 + nF^-$$

type may be calculated from this figure and from the values of the dissociation constants of complex fluorides of beryllium.

For the equilibrium: $BeF_4^{--} + 2OH^- = Be(OH)_2 + 4F^-$

we have: $$K_{equil.} = \frac{[F^-]^4}{[BeF_4^{--}][OH^-]^2} = \frac{[Be^{++}][F^-]^4}{[BeF_4^{--}]} \cdot \frac{1}{[Be^{++}][OH^-]^2} = \frac{K'_{BeF_4^{--}}}{Lp_{Be(OH)_2}},$$

where $K'_{BeF_4^{--}}$ is the aggregate dissociation constant of BeF_4^{--} (as distinct from $K_{BeF_4^{--}}$, the step-by-step dissociation constant.

Hence: $$K_{equil.} = \frac{K_{BeF^+} \cdot K_{BeF_2} \cdot K_{BeF_3^-} \cdot K_{BeF_4^{--}}}{Lp_{Be(OH)_2}} = \frac{4.16 \cdot 10^{-17}}{2.1 \cdot 10^{-15}} = 0.0198.$$

For the equilibrium $BeF_3^- + 2OH^- \rightleftarrows Be(OH)_2 + 3F^-$, we have: $K_{equil.} = 1.94$ and

likewise: $BeF_2 + 2OH^- \rightleftarrows Be(OH)_2 + 2F^-$, $K_{equil.} = 7000$;

$BeF^+ + 2OH^- \rightleftarrows Be(OH)_2 + F^-$ $K_{equil.} = 6.2 \cdot 10^8$

Hence, the equilibrium in the reaction $BeF_n^{(2-n)} + 2OH \rightleftarrows Be(OH)_2 + nF^-$ for $\underline{n} = 1$ and 2 must be strongly shifted toward the formation of $Be(OH)_2$, whereas at $\underline{n} = 3$ and 4 (especially at $\underline{n} = 4$), the reaction between the complex hydroxyl and fluoride ions of beryllium should be largely suppressed. Comparison of the values of the reaction equilibrium constants for:

$$BeF_n^{(2-n)} + 2\,OH^- \rightleftarrows Be(OH)_2 + nF^-,$$

$$AlF_n^{(3-n)} + 3\,OH^- \rightleftarrows Al(OH)_3 + nF^-,$$

at various values of $\underline{n}$ indicates that the complex fluorides of beryllium ought to resist the action of hydroxyl ions better than the complex fluorides of aluminum [4], notwithstanding the fact that the latter are more stable than the former. This is due to the fact that the difference between the values of Lp for aluminum and beryllium hydroxides ($Lp_{Al(OH)_3} = 4.7 \cdot 10^{-18}$) is much greater that the difference between the respective dissociation constants.

Thus, the precipitation of beryllium hydroxide cannot be quantitative in the presence of an excess of sodium fluoride, and it must be harder to effectuate than the precipitation of aluminum hydroxide from solutions of complex fluorides of aluminum [4].

These conclusions are confirmed by the experimental results, which were obtained as follows. We prepared a number of mixtures, each containing 10 ml of a 0.1 molar solution of beryllium nitrate,[*] and various quantities of a 0.1 molar solution of sodium fluoride. The volume of each mixture was brought up to 100 ml by adding water. After this, all the solutions were titrated back against phenolphthalein with a solution of sodium hydroxide ($K_{NaOH} = 0.0787$).

Column 4 of Table 2 indicates the phase differences found to exist in the solutions after titration with a solution of sodium hydroxide.

TABLE 2

1 Solution No.	2 $\frac{NaF}{Be(NO_3)_2}$	3 Volume of NaOH solution (K = 0.0787), in ml, required for titration against phenolphthalein	4 Formation of a precipitate
1	Only $Be(NO_3)_2$	24.5	$Be(OH)_2$
2	1	22	Nearly the same volume of precipitate as in solution No. 1.
3	2	15.5	Less precipitate than in Solution No. 2.
4	3	8	Very little precipitate
5	4	2.5	No precipitate
6	5	2.5	No precipitate

It must be noted that the solution of the beryllium preparation in water after sodium fluoride has been added will exhibit an alkaline reaction (coloring phenolphthalein) if the beryllium preparation contains a trace of a basic salt, thus causing the formation of a certain amount of amorphous precipitate.

This may be the result of the following reactions:

$$Be(OH)NO_3 + NaF \rightleftarrows BeFNO_3 + NaOH,$$

$$Be(OH)NO_3 + NaOH \rightleftarrows Be(OH)_2 + NaNO_3.$$

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[*] The beryllium nitrate solution was prepared from beryllium carbonate by dissolving the latter in nitric acid. The nitric acid was taken in some excess over the calculated quantity. This is indicated by the acidity of the solution (pH = 1.28) and by the constant volume of a solution of sodium hydroxide (2.5 ml of Solutions Nos. 5 and 6, Table 2) required for titration against phenolphthalein in the presence of an excess of sodium fluoride, i.e., when all the beryllium is in solution as complex fluoride ions.

Thus we may conclude that fluorine ions displace hydroxyl ions from the molecule of the basic salt. These reactions may be employed to detect traces of a basic salt in preparations of beryllium as well as, possibly, in preparations of some other metals.

SUMMARY

1. A study has been made of the equilibrium:

$$Be^{++} + FeF^{++} + (SCN)^- \rightleftarrows BeF^+ + Fe(SCN)^{++},$$

by means of measuring the optical density of solutions with a fixed value of the dissociation constant of complex monofluoride ions of beryllium:

$$K_{BeF^+} = \frac{[Be^{++}][F^-]}{[BeF^+]} = 1.3 \cdot 10^{-6}.$$

2. The values of the step-by-step dissociation constants have been calculated:

$$K_{BeF_2} = \frac{[BeF^+][F^-]}{[BeF_2]} = 1.14 \cdot 10^{-5}; \quad K_{BeF_3^-} = \frac{[BeF_2][F^-]}{[BeF_3^-]} = 2.75 \cdot 10^{-4};$$

$$K_{BeF_4^{--}} = \frac{[BeF_3^-][F^-]}{[BeF_4^{--}]} = 1 \cdot 10^{-2}.$$

The product of four step-by-step constants (the aggregate dissociation constant of BeF_4^{--} according to $BeF_4^{--} \rightleftarrows Be^{++} + 4F^-$) is:

$$K = \frac{[Be^{++}][F^-]^4}{[BeF_4^{--}]} = K_{BeF^+} \cdot K_{BeF_2} \cdot K_{BeF_3^-} \cdot K_{BeF_4^{--}} = 4.16 \cdot 10^{-17}.$$

3. Theresistance of complex fluorides of beryllium to an aqueous nitric-acid solution (0.1 N HNO_3) lies in between that of the complex fluorides of iron (III) and aluminum. The monofluoride complex ions of these metals may be arranged in the following series in order of increasing stability:

FeF^{++}	BeF^+	AlF^{++}
$K = 5 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	$0.5 \cdot 10^{-6}$.

4. The values of the equilibrium constant of the equation

$$BeF_n^{(2-n)} + 2\,OH^- \rightleftarrows Be(OH)_2 + nF^-$$

have been computed for n = 1, 2, 3, or 4.

5. Some conclusions have been reached concerning the quantitative determination of beryllium.

6. It has been found that the reaction $Be(OH)NO_3 + NaF \rightleftarrows BeFNO_3 + NaOH$ may be employed to detect traces of a basic salt in beryllium preparations.

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THE TEMPERATURE COEFFICIENTS OF THE HEATS OF SOLUTION OF ELECTROLYTES.

THE HEATS OF SOLUTION OF KCl IN WATER AT 50° AND OF $MgSO_4 \cdot 7H_2O$ IN WATER AND IN Na_2SO_4 SOLUTIONS AT 25, 35 AND 45°.

Yu. Ya. Kaganovich and K. P. Mishchenko

In this paper the authors make a thorough analysis of the temperature coefficients of the heats of solution ΔH_m of electrolytes in an endeavor to establish a link between the observed patterns of behavior and the structural peculiarities of the solutions at various concentrations.

Inasmuch as the material in the literature on the determination of the temperature coefficients ΔH_m is not very extensive (cf. below) a study was made of the integral heats of solution in water of KCl at 50° and of $MgSO_4 \cdot 7H_2O$ at 25°, 35° (a single point), and 45°, in order to expand the available body of data.

The heats of solution have been fairly well investigated for KCl throughout all concentration ranges at 25° [1], and up to m = 0.342 mol per 1000 g H_2O at 12.5° [2]. Figures were recently published by Voskresenskaya and Ponomareva [3] for 75°, appearing after the completion of our researches.

Up to the completion of our research no figures have been available for $MgSO_4 \cdot 7H_2O$, indicating the variation of ΔH_m with the temperature and concentration. The only experimental data available has been the heats of solution at 18°, contained in the summary by Bichowsky and Rossini [4], these figures being the result of recomputation and combination of episodic values obtained by various authors for a limited number of concentrations. After the publication of our results in Kaganovich's dissertation, there appeared the paper by Voskresenskaya and Yankovskaya [5], in which the heats of solution of $MgSO_4 \cdot 7H_2O$ are also given for 25° over a wide range of concentrations.

In our evaluation we have made use of both sets of figures, preferring the results obtained by Vosnesensky and Yanovskaya [5] for high concentrations and our figures for more dilute solutions, inasmuch as we have made a number of improvements in the calorimetric apparatus [6] during our investigations of these solutions, while, in the region of very high dilutions our ΔH_m curve is closer to the curve given by Lange and Streek [7] for the heats of dilution, obtained with the Lange ultracalorimeter.

Heats of Solution of KCl at 50°

The chemically pure KCl was purified by double recrystallization; this was quite enough for calorimetric purposes [8].

The results of our measurements are listed in Table 1. Inasmuch as the precision of measurement has been discussed more than once in the publications originating in our laboratory [9], and this present case involved no special features of computational procedure or of the handling of the experimental data, we have listed in the table only the final values of the integral heats of solution. They were obtained directly in some cases, while in others they were computed from the intermediate heats of solution of weighed samples of the salt in salt solutions.

TABLE 1

Integral Heats of Solution ΔH_m for KCl in Water at 50°
(Plus sign = Absorption of Heat)

Mols of salt per 1000 g of H_2O	ΔH_m, cal per mol of salt	Mols of salt per 1000 g of H_2O	ΔH_m, cal per mol of salt	Mols of salt per 1000 g of H_2O	ΔH_m, cal per mol of salt
0.138	3420	0.521	3380	2.216	3256
0.274	3408	0.826	3353	2.828	3249
0.415	3393	1.110	3351	3.325	3205
0.467	3383	1.666	3310	3.877	3226
				4.436	3210
				4.744	3212

Heats of Solution of $MgSO_4 \cdot 7H_2O$ at Three Temperatures

The $MgSO_4 \cdot 7H_2O$ was prepared by recrystallizing the chemically pure salt from an aqueous solution acidulated with a single drop of sulfuric acid. The salt crystals were desiccated to constant "free flowing" through a funnel when subjected to air suction. The salt contained 51.53% water (the theoretical figure should be 51.16%). The salt was kept in an exsiccator above a solution of sulfuric acid with the corresponding vapor tension.

TABLE 2

Integral Heats of Solution of $MgSO_4 \cdot 7H_2O$ in Water at 25, 35, and 45°
(Plus sign = Absorption of Heat)

Mols of salt $MgSO_4$ per 1000 g H_2O	ΔH_m, cal per mol of salt	Mols of salt $MgSO_4$ per 1000 g H_2O	ΔH_m, cal per mol of salt	Mols of salt $MgSO_4$ per 1000 g H_2O	ΔH_m, cal per mol of salt
25°					
0	3080	0.187	3883	0.950	4233
0.0024	3116	0.231	3996	1.237	4325
0.0087	3260	0.311	4018	1.576	4370
0.0180	3389	0.363	4020	1.773	4428
0.0340	3546	0.477	4082	1.946	4470
0.0805	3762	0.643	4164	2.110	4510
0.110	3838	0.788	4201	2.230	4540
0.126	3850				
35°					
0.114	3852	-	-	-	-
45°					
0.111	3847	0.225	4051	0.286	4120
0.140	3860	0.248	4105	0.311	4110
				0.350	4160

Table 2 gives the final values of the integral heats of solution for three temperatures. With the heats of dilution mentioned above [7] we computed the heats of solution at 25° for the regions of high dilution as well, which enabled us to find the initial heat of solution ΔH_0.

Heats of Solution of $MgSO_4 \cdot 7H_2O$ in Aqueous Solutions of Na_2SO_4 at Three Temperatures

Since several authors have commented on the analogy between the effect of temperature upon the energetic properties of solutions and the presence in the solvent of a previously dissolved different salt, we measured the heats of solution of $MgSO_4 \cdot 7H_2O$, at a constant concentration m, of 0.139 mol per 1000 g H_2O in Na_2SO_4 solutions of varying concentrations. These experiments were also conducted at three temperatures.

The final results of these measurements are listed in Table 3.

TABLE 3

Integral Heats of $MgSO_4 \cdot 7H_2O$ ($m = 0.139$) in Aqueous Solutions of Na_2SO_4 of Varying Concentrations at 25, 35, and 45°

Concentration of Na_2SO_4 in the solution, mols per 1000 g H_2O	ΔH_m, cal per mol $MgSO_4 \cdot 7H_2O$	Concentration of Na_2SO_4 in the solution, mols per 1000 g H_2O	ΔH_m, cal per mol $MgSO_4 \cdot 7H_2O$
25°		35°	
0	3850	0	3852
0.417	3860	1.176	3990
0.633	3870	2.717	4120
0.914	3885	45°	
1.162	3893	0	3858
2.134	3900	0.828	4070
2.787	3936	1.547	4295

Temperature Coefficients of the Heats of Solution of Electrolytes

As we have already stated, the experimental material suitable for indicating the variation of the heats of solution of electrolytes with temperature is relatively scarce. In addition to the aforementioned data for KCl and $MgSO_4 \cdot 7H_2O$, only data for a few electrolytes is available. Many of the older values are useless, inasmuch as the errors of measurement exceed the differences in ΔH_m at various temperatures that concern us here. The work of Graham [10], for instance, who was apparently the first to establish the increase in the exothermicity of ΔH_m with rising temperature, is only of historical interest. The papers of Person [11], Berthelot and Ylosvay [12], Pickering [13], Tilden [14], Winkelmann [15], and the like, are too inaccurate to meet modern needs.

Moreover, all these authors studied the heats of solution at only one, and sometimes two, concentrations, even though for several temperatures. Henceforth we enumerate only the later researches, the data of which we found usable for evaluation after having subjected it to critical analysis.

For NaCl solutions we employed the 25° isotherm plotted by Wust and Lange [1], and the 50° isotherms plotted by Voskresenskaya [16] and Voskresenskaya and Yanovskaya [5]. Then there is a single value of ΔH_m for a concentration m of 0.370, at 75°, reported by Voskresenskaya and Yanovskaya [3].

As for KNO_3 solutions, we were able to make use of the reliable sections of the

12.5 and 25° isotherms plotted by Lange and Monheim [2], as well as the three points (25, 50, and 75°) recorded by Voskresenskaya and Yanovskaya [3] for a concentration $\underline{m}$ of 0.185.

The values of ΔH_m for KNO_3 reported by Roth and Eymann [17] at 15.2, 21, 29.8, and 50.8° and by Beranger-Calvet [18] at 14.7° regularly express the variation of ΔH_m with concentration and temperature, but the exothermicity of the heat values is somewhat smaller (by some 50 calories) than the precise values reported by Lange and Monheim [2].

All the foregoing electrolytes dissolve with the absorption of heat. Among the electrolytes that dissolve with the evolution of heat, we have been able to include Na_2SO_4, HNO_3, HCl and (for a single concentration) $MnCl_2 \cdot 4H_2O$.

An isotherm for Na_2SO_4 at 11° can be plotted from Perren's data [19] as recomputed by Voskresenskaya and Yanovskaya; at 18° from the tables of Bichowsky and Rossini; and at 50° from the paper by Voskresenskaya and Yanovskaya [5]. Moreover, there are two reliable points – at 25° and 50° – for a concentration $\underline{m}$ of 0.185 in the work of Voskresenskaya and Ponomareva [20,3].

Mishchenko's results of measurements at 40° [21], the data in the tables published by Bichowsky and Rossini [4] for 18°, and three points for three concentrations at 25° in the paper by Forsyte and Giaque [22] were employed in our analysis of the variation of the heats of solution of HNO_3 with temperature. The variation of the heats of solution of HCl with temperature at 3.6, 21.5, 42, and 62.3° is described accurately enough in the paper by Vrevsky and Zavaritsky [23]. We have two reliable points at 25 and 50° for $MnCl_2 \cdot 4H_2O$ at a concentration $\underline{m}$ of 0.185 in the papers by Voskresenskaya and Ponomareva [20,3].

Thus, we considered four electrolytes that dissolve with the absorption of heat (KCl, NaCl, $MgSO_4 \cdot 7H_2O$, and KNO_3) and four that dissolve with the evolution of heat (Na_2SO_4, HNO_3, HCl, and $MnCl_2 \cdot 4H_2O$). At the same time they represent all three of the classes mentioned by Mishchenko and Pronina in their classification of electrolytes according to the shape of the curves showing the variation of the heats of solution with the concentration [9,5].

In all observed instances, the integral heat of solution becomes more exothermic as the temperature is raised, which fully agrees with the findings of various authors who made episodic observations of the variation of ΔH_m with temperature.

The apparent exceptions to this rule constituted by the behavior of $MgSO_4 \cdot 7H_2O$ and (in part) that of HNO_3 have been interpreted by us below; they are merely further confirmations of the general rule.

Thermodynamic considerations. We shall begin our discussion with a review of some general undisputed thermodynamic conclusions. As we know, the temperature coefficients of the heats of solution are related to the specific heats by the First Law as follows.

For integral heat of solution:

$$\frac{d\Delta H_m}{dT} = C_p \begin{array}{l}\text{of the solution}\\ \text{containing 1 mol}\\ \text{of the electrolyte}\\ + \underline{n} \text{ mols } H_2O\end{array} - \left(C_p \begin{array}{l}\text{of the}\\ \text{solid}\\ \text{salt}\end{array} + nC_{p H_2O} \right) = \varphi_{c_p} - C_p \begin{array}{l}\text{of the}\\ \text{solid}\\ \text{salt}\end{array} \qquad (1)$$

while for the partial case of the first heat of solution:

$$\frac{d\Delta H_0}{dT} = \bar{C}^{o}_{p_2} - C_{p} \text{ of the solid salt} \qquad (1a)$$

Where C_p = the corresponding index of the molecular heat,

φ_{c_p} = the apparent molar heat capacity of the salt in solution,

$\bar{C}^{o}_{p_2}$ = the partial molar heat capacity of the salt in an infinitely dilute solution,

$\underline{n}$ = the number of mols of water per mol of the electrolyte at the given concentration $\underline{m}$.

For the differential heats of dilution and solution (the relative partial molar heat contents of the solution components) $\bar{L}_1$ and $\bar{L}_2$:

$$\frac{d\bar{L}_1}{dT} = \bar{C}_{p_1} - \bar{C}^{o}_{p_1} = \bar{C}_{p_1} - C_{pH_2O} \qquad (2)$$

$$\frac{d\bar{L}_2}{dT} = \bar{C}_{p_2} - \bar{C}^{o}_{p_2} = \bar{C}_{p_2} - \varphi^{o}_{c_p}, \qquad (2a)$$

where $\bar{C}_{p_1}$ and $\bar{C}_{p_2}$ are the partial molar heat capacities of water and the electrolyte, respectively, in a solution of the given concentration $\underline{m}$; $\bar{C}^{o}_{p_1} = C_{pH_2O}$ is the molar capacity of pure water; and $\bar{C}^{o}_{p_2}$ is the partial molar heat capacity of the electrolyte in an infinitely dilute solution.

It follows from Equation (1) that for salt solutions the temperature coefficients ΔH_m must be negative, as a rule, i.e., ΔH_m must become more exothermic as the temperature is raised. This follows from the fact that when electrolytes are dissolved in water, the heat capacity of the solution, at low and medium concentrations, is always below not only the total heat capacity of the salt and water, but as a rule even below the heat capacity of the water in the solution. The apparent molar heat capacity of the salt in solution is usually negative, $\varphi_{c_p} < 0$, and though it may become positive at high concentrations (as in the case of $CaCl_2$ solutions, for instance), $\varphi_{c_p} < C_p$ of the solid salt.

The only exceptions to this rule that we know of are the highly concentrated solutions of strong acids in water, which should, however, be more properly treated as solutions of water in the acid.

In this case φ_{c_p} attains fairly large positive values, and the temperature coefficients ΔH_m change sign at a certain concentration.

$\frac{d\bar{L}_1}{dT}$ and $\frac{d\bar{L}_2}{dT}$ may be of different signs:

$\frac{d\bar{L}_1}{dT} < 0$ at $\bar{C}_{p_1} < C_{pH_2O}$, and

$\frac{d\bar{L}_1}{dT} > 0$ at $\bar{C}_{p_1} > C_{pH_2O}$.

The derivatives $\frac{d\bar{L}_2}{dT} < 0$ at $\bar{C}_{p_2} - \bar{C}^{o}_{p_2} < 0$ or at $\bar{C}_{p_2} < \varphi^{o}_{c_p}$; $\frac{d\bar{L}_2}{dT} > 0$ at

$\bar{C}_{p2} - \bar{C}^{o}_{p2} > 0$ or at $\bar{C}_{p2} > \varphi^{o}_{c_p}$.

Other cases are also encountered. The temperature functions $\bar{L}_1$ and $\bar{L}_2$ are of particular interest from the practical point of view as well, since they enable us to find the change in activity of water and of the electrolyte with temperature, inasmuch as:

$$\frac{d \ln a_1}{d T} = - \frac{\bar{L}_1}{RT^2} \cdot \quad (3) \qquad \text{in the general case.}$$

Interpretation of the variation of the heats of solution and dilution with temperature. The first heat of solution ΔH_0 may be represented, as we know, by the equation:

$$\Delta H_0 = \Delta H_{\text{lattice}} + \Delta H^{\pm}_{h_1 m = 0} .$$

Here all the exothermic and endothermic effects that are not related to the heat of destruction of the crystal lattice are formally part of the aggregate heat of solvation of the ions $\Delta H^{\pm}_{h_1 m = 0}$. Within the limits of accuracy involved here, we may consider the lattice heat to be independent of the temperature. A preliminary calculation shows that within the range 20-50° the quantity $d\Delta H_{\text{lattice}}/dT$ is less than 1/20 of the total probable error in the absolute values of $\Delta H_{\text{lattice}}$. Thus, all the observed effect of temperature upon $\Delta H_{m = 0}$ must be assigned to changes in $\Delta H^{\pm}_{h_1 m = 0}$ with temperature.[*] In all the observed cases, the first heat of solution becomes more exothermic as the temperature rises, since $\bar{C}^{o}_{p2}$ is negative. The solvation of ions, like the exothermic process as a whole, must decrease as the temperature rises (probably from the energy standpoint, though not from the coordination standpoint, in an infinitely diluted solution[**]). That is why the increase in exothermicity ΔH_0 can be explained only by a decrease in some endothermic term entering into $\Delta H^{\pm}_{h_1 m = 0}$. The individual components of $\Delta H^{\pm}_{h_1 m = 0}$ are given and computed in the paper by Mishchenko and Sukhotin dealing with the problem of ionic solvation [24]. Three basic endothermic effects contribute to the overall total: $\underline{1}$ - the effect of decomposition of water; $\underline{E}_{\text{rep}}$ - an effect related to the Born repulsion of dipoles and ions in the solvate shell; and $\underline{C}$ - the effect of repulsion between the water dipoles in the solvate shell. All of these three effects ought to diminish with rising temperature. The first effect diminishes as the result of a change in the structure of water (in the sense of the Bernal and Fowler model) in the direction of the form transformation I → II → III, which is borne out by numerous X-ray photos, analysis of the Mandelstam - Landsberg - Raman spectra, etc. (cf, for exaple, the table in [6]). The terms E_{rep} and C must also become numerically smaller owing to an increase in the distances and the effect of thermal motion. But these terms are small in comparison to l, and their changes are, to be sure, masked by the corresponding changes in the exothermic effects. The l term possesses the largest absolute value. Its change with temperature may be approximately estimated by the temperature coefficient of the heat of evaporation of water: $\frac{d\lambda}{dT} \simeq C_{p_{steam}} - C_{p_{liquid}} \cong 8 - 18 \cong - 10$ cal per deg. mol

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[*] It may be objected that $\frac{d\Delta Hm}{dT}$ might be better treated by interpreting the heat capacities that govern it according to Equation (1). But the theory of the specific heats of electrolyte solutions is quite incomplete at present for the region of medium and high concentrations and has gotten into a blind alley to a certain extent in recent years. Moreover, we know ΔHm and $\frac{d\Delta Hm}{dT}$ with a higher degree of precision than we know φ and c_p, and their interpretation in the region of undiluted solutions is easier.

[**] The mechanism of the change in solvation with temperature and concentration has been investigated in detail by Mishchenko in a paper dealing with the solvation of ions [24]. Definite and differing coordination numbers (in contrast to the practice of previous authors) have been assigned to all ions. A calculation has been made of the solvation energy, allowing for the individual links in this process. The change in solvation as a function of $\underline{T}$ and $\underline{m}$ is considered from the standpoint of energy desolvation (diminution of the stability of the solvate complex) and coordination desolvation (diminution of the number of molecules of water bound up with the ion).

This quantity, multiplied by the sum of the coordination numbers of the cation and the anion, yields a product ranging from -100 to -160 cal per degree-mol, which is fully commensurable with the magnitude of the temperature coefficients observed for ΔH_o (-20 to -70 cal per degree-mol), if we bear in mind the partial compensation due to the diminution of the exothermic terms of the heat of solvation with temperature.

It is very much harder to decipher the integral heat of solution for terminal, and particularly, for high concentrations. Considering, as before, that the heat content of the solid salt is practically independent of the temperature, we must seek an explanation of the temperature coefficients in the changes of the composition of the water and ions in the solution with temperature. The following may be stated: when a solution is heated: 1) the energy solvation must decrease and, at high concentrations and temperatures, the coordination solvation as well, which ought to make ΔH_m less exothermic; 2) the energy required for breaking down the primary structure of the water to form solvate complexes must diminish, inasmuch as the water is already "predecomposed" by the action of the temperature; this factor ought to make ΔH_m more exothermic; and 3) in concentrated solutions a rise in temperature must diminish the exothermic effects, due, in the case of some electrolytes, to the possible formation of "ionic vapors" or even of undissociated moleculles, which would make ΔH_m less exothermic. In our opinion, this effect can make itself felt only in weak electrolytes, possessing high heats of dissociation. It doubtless plays a subrodinate role in the examples we have been discussing.

Thus, we come to the conclusion that the negative temperature coefficients ΔH_m and ΔH_m^{∞} can be explained solely by the fact that the diminution, with rising temperature, of the quantity of heat required to break down the structure of water during the dissolution of electrolytes predominates over the rise in the endothermicity caused by a diminution in the exothermic members of the solvation effect. This proposition, first stated in an indirect form by Holutta and Werner [25] and Drucker [26] in connection with a discussion of the changes in ΔH_m produced by dissolving one salt in a ready solution of another, was proven by Mishchenko in a lecture delivered in March, 1944 [27]. A paper by Voskresenskaya and Ponomareva appeared later in 1944 [20], followed in 1947 by the dissertation of Kaganovich, in which a similar point of view was developed.

If this hypothesis is true, it must be expected that:

1) The temperature coefficients ΔH_m will be negative. A positive value for them would require special explanation;

2) As the temperature rises, these temperature coefficients must become less negative (less exothermic), i.e., the second derivative of ΔH_m with respect to temperature must be positive, as a rule. This follows from the fact that the endothermic effects of the further breakdown of water already "predecomposed" by heat must be smaller, of course. The latter circumstance, which is confirmed by the temperature coefficients of a number of other properties of solutions, has not been noticed by anyone else before this;

3) As the electrolyte concentration rises, with the temperature held constant,

the temperature coefficients ΔH_m must likewise become less negative (less exothermic), inasmuch as the initial batches of the salt to be dissolved act like the temperature, as it were, "predecomposing" the structure of the water, which must end up by diminishing the weight of the exothermic member and relatively increasing the weight of the temperature dehydration. In highly soluble salts, it is possible, even probable, that the sign of the coefficient changes in the region of extremely high concentrations. Unfortunately, the accumulation of experimental material that might confirm the latter hypothesis is still in the planning stage of our research.

4) When a salt is not dissolved in pure water, but in a ready solution of another electrolyte, the temperature coefficients ΔH_m of the electrolyte being dissolved must likewise become less negative, since the preliminarily dissolved salt acts as the temperature, "predecomposing" the water. Here, too, we may expect the sign to change at a sufficiently high concentration of the salt constituting part of the solvent. Such a change in sign has actually been observed in the paper by Holutta and Werner [25] in the example of dissolving KNO_3 up to a constant concentration of 0.178N in KCl solutions of varying concentrations (from 0 to 2.5 N). In the case of electrolytes containing strongly hydrated ions, which regulate the structure of the water, these coefficients may even be positive throughout the range of concentrations. The marked endothermic effect of the desolvation of the electrolyte as its concentration or that of a previously dissolved salt rises will predominate over the exothermic term as a result of the negligible rupture of the structure of the water.

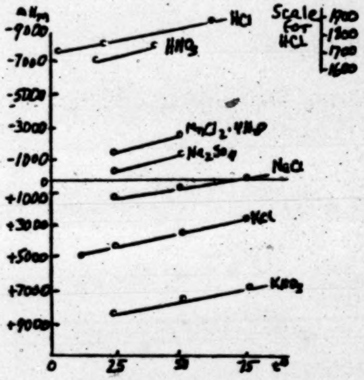

Fig. 1. Integral heats of solution as a function of temperature.

For all the salts except NaCl and for the acids, the concentration of the dissolving electrolyte is:

$m = 0.185$ mol per 1000 g H_2O

For NaCl:

$m = 0.370$ mol per 1000 g H_2O

We cite below the data of our own as well as those contained in the literature, which fully bear out the hypothesis expressed above and its corollaries.

Fig. 1 is a schematic picture of the variation of ΔH_m with the temperature for seven electrolytes. The data for all the electrolytes, with the exception of NaCl, refer to a concentration m of 0.185. The concentration for NaCl is 0.370 mol per 1000 g of water. The ΔH_m becomes more exothermic with rising temperature for all the substances examined.

Table 4 gives the values of ΔH_m for KCl and their mean temperature coefficients in the temperature range from 12.5 to 75°. This system is the one that has been most extensively investigated at various temperatures and concentrations.

The derivatives become less negative for all concentrations as the temperature is raised. They undergo practically no change when the concentration is increased in the region of high dilutions. Apparently, what happens here is the relatively small destructive action of KCl on the water.

TABLE 4

Temperature Coefficients and Integral Heats of Solution of KCl in Water at 12.5, 25, 50, and 75°, According to Lange and Monheim, Lange and Wust, Kaganovich and Mishchenko, and Voskresenskaya and Ponomareva (Interpolated)

Concentration		ΔH_m				$\frac{d\Delta H_m}{dT}$		
mols of salt per 1000 g H_2O	mols of salt per 100molsH_2O	12.5°	25°	50°	75°	12.5-25°	25-50°	25-75°
0	0	4650	4119	-	-	42.4	-	-
0.055	0.1	4695	4190	3430	-	40.4	30.0	-
0.11	0.2	4693	4197	3420	-	39.6	31.2	-
0.16	0.3	4687	4198	3410	2609	39.1	31.2	31.7
0.22	0.4	4675	4198	3410	-	38.1	31.2	
0.28	0.5	4669	4195	3408	-	37.9	31.4	
0.33	0.6	4654	4189	3397	-	37.2	31.6	
0.55	1.0	-	4160	3382	-	-	31.1	
1.11	2.0	-	4123	3351	-	-	30.8	
1.66	3.0	-	4043	3310	-	-	29.3	
1.22	4.0	-	3966	3253	-	-	28.5	
2.77	5.0	-	3894	3247	-	-	25.8	
3.33	6.0	-	3828	3200	-	-	25.1	
3.88	7.0	-	3770	3200	-	-	22.8	
4.44	8.0	-	3720	3200	-	-	20.8	
4.82	8.68	-	3692	3200	-	-	19.6	

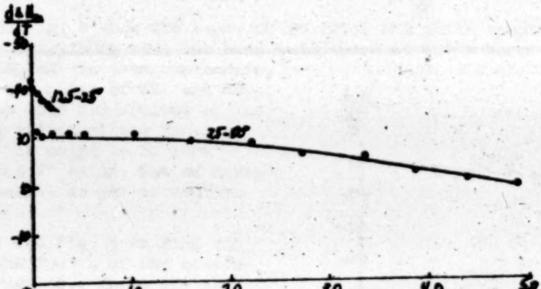

Fig. 2. Temperature coefficients of the integral heats of solution of KCl in water.

At higher concentrations a systematic diminution sets in from -31 to -19 cal per degree-mol. This function is shown graphically in Fig. 2.

The NO_3' ion has been often described as a powerful "disrupter" of the structure of water. In Table 5 and Fig. 3 we see a new confirmation of this: an appreciable decrease in the negativeness of $d\Delta H_m/dT$ begins at an m of 0.0065 for KNO_3.

TABLE 5

Temperature Coefficients and Integral Heats of Solution of KNO_3 in Water at 12.5 and 25°, According to Lange and Monheim, and at 25, 50, and 75°, According to Voskresenskaya and Ponomareva

Concentration		ΔH_m 12.5°	ΔH_m 25°	$\frac{d\Delta H_m}{dT}$ 12.5-25°
Mols of salt per 1000 g H_2O	Mols of salt per 100 mols of H_2O			
0	0	8896	8379	-41.3
0.0004	0.0007	8899	8385	-41.3
0.0036	0.0065	8903	8395	-40.6
0.0064	0.0116	8902	8401	-40.1
0.0325	0.0586	8879	8392	-39.0
0.0486	0.0876	8861	8381	-38.4
0.068	0.123	8837	8366	-37.7
0.090	0.163	8809	8346	-37.0
0.116	0.210	8780	8326	-36.3
0.145	0.262	8749	8304	-35.6
		$\Delta H_{m25°}$	$\Delta H_{m50°}$	$\Delta H_{m75°}$ $\frac{d\Delta H_m}{dT}$
0.183	0.33	8185	7590	6928 (50-75°) -26.4 (25-50°) -23.8

Table 6 and Fig. 4 show the heats of solution and their temperature coefficients for NaCl. Everything that has been said above is fully borne out in this case as well. $d\Delta H_m/dT$ is less exothermic, however, than in the cases of KCl and KNO_3, which fully agrees with our notions of the slight disrupting effect of the $Na^{\cdot}$ ion upon water [25]. It ought to be even smaller for $Li^{\cdot}$ and F' salts, but we haven't the necessary material as yet to confirm this.

In Table 7 and Fig. 5 we find the confirmation of the fourth of the conclusions stated on Page 36. These are the data of Holutta and Werner [25] on ΔH_m and their temperature coefficients, as observed for the dissolution of KCl in KNO_3 solutions and vice versa, as converted by us. The propositions we stated are fully borne out: the derivatives become less and

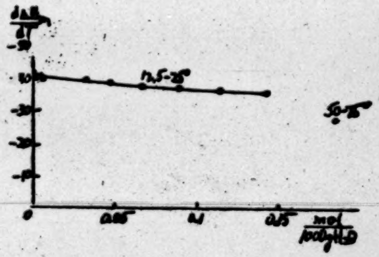

Fig. 3. Temperature coefficients of the integral heats of solution of KNO_3 is water.

TABLE 6

Temperature Coefficients and Integral Heats of Solution of NaCl in Water at 25, 50, and 75°, According to Lange and Wust and Voskresenskaya and Yankovskaya, (Interpolated)

Concentration		ΔH_m	ΔH_m	ΔH_m	$\frac{d\Delta H_m}{dT}$	$\frac{d\Delta H_m}{dT}$	$\frac{d\Delta H_m}{dT}$
Mols of salt per 1000 g H_2O	Mols of salt per 100 mols of H_2O	25°	50°	75°	25-50°	50-75°	20-25°
0	0	1066	–	–	–	–	–
0.33	0.6	1044	444	-117	-24.0	-22.4	-27.0 *
0.55	1.0	979	435	–	-22.1		
1.11	2.0	892	420	–	-18.8		
1.56	3.0	805	390	–	-16.6		
2.21	4.0	725	350	–	-14.0		
2.77	5.0	655	340	–	-12.6		
3.32	6.0	598	310	–	-10.3		
3.88	7.0	550	350	–	- 8.0		
4.43	8.0	510	360	–	- 6.0		
4.98	9.0	479	370	–	- 4.0		
5.55	10.0	458	486	–	- 1.0		

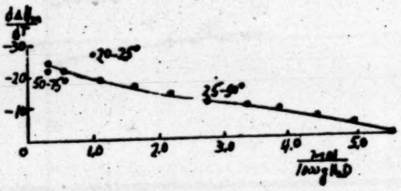

Fig. 4. Temperature coefficients of the integral heats of solution of NaCl in water.

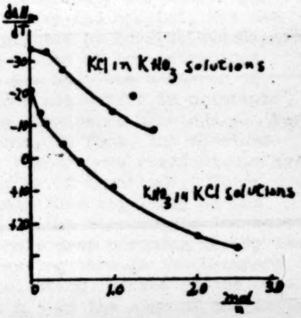

Fig. 5. Temperature coefficients of the integral heats of solution of KCl in KNO_3 solutions and of KNO_3 in KCl solutions.

less negative as the concentration of the salt that is part of the solvent is increased, the derivative $d\Delta H_m/dT$ changing sign and attaining a rather high positive value for the dissolution of KNO_3 in KCl solutions. Thus, desolvation predominates in this case; this may be due to the fact that the system is already close to the "boundary of complete solvation." **

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*Taken from the paper by Cohen and Kooy [28], who measured ΔHm at 20 and 25° for a single concentration m of 0.55.

**Mishchenko [29] uses this term to denote the concentration at which the number of mols of water required for 1 mol of the salt is exactly equal to the sum of the coordination numbers for anion and cation solvation. Above this concentration there are not enough water molecules present for complete solvation, and they begin to compete for the solvent, thus causing coordination desolvation to set in.

Up to this point we have considered salts whose dissolution involves an endothermic effect. Figure 6 gives the heats of solution as a function of the concentration at various temperatures for all the salts we have considered and for Na_2SO_4, which dissolves with the evolution of heat. Figure 6 indicates that everything that has been stated above is borne out in the case of this exothermic salt as well.

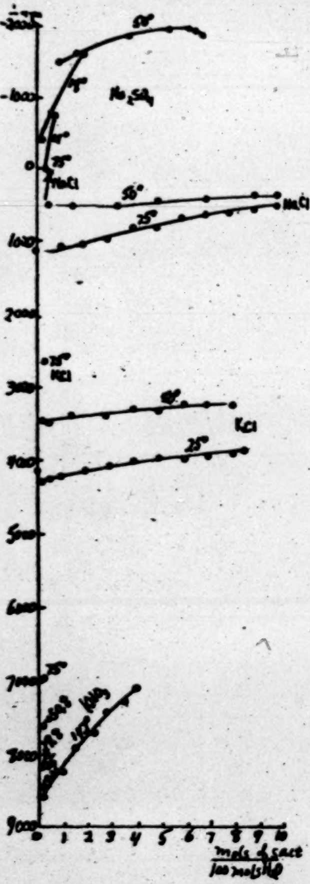

Fig. 6. Integral heats of solution of salts.

The HNO_3 - H_2O system, which has been investigated by Mishchenko [21], requires special consideration. Here solutions of all compositions are possible, from 100% water to 100% acid. Hence, the boundary of complete solvation lies almost at the beginning of the solid curve, and the structures of the solutions are quite peculiar in the regions of medium and high concentrations. Concentrated solutions of HNO_3 in water should be regarded as solutions of water in the acid. In this connection, the curve showing the variation of the temperature coefficients ΔH_m with concentration is also peculiar.

Table 8 and Fig. 7 give the heats of solution and their temperature coefficients for this acid according to the data published by Mishchenko, the tables published by Bichowsky and Rossini, and the three points plotted by Forsyte and Giaque [22]. In the region of concentrations ranging up to $\underline{m} = 23$,[*] the behavior of this system does not differ in principle from the cases considered previously. For dilute solutions, in fact, the absolute values of the temperature coefficients are of the same order of magnitude. Their exothermicity diminishes regularly as the concentration of the electrolyte increases, the slope of this drop becoming merely less steep after passing through the boundary of complete solvation, marked on the diagram.[**] But at $\underline{m} = 23$ the sign of the derivative changes to positive, i.e., the endothermic changes predominate during heating. To judge from the curve, the course of the changes with temperature are likewise normal for the concentrations $\underline{m} = 0$, and $\underline{m} = 18.5$ (cf the temperature curves in Fig. 7).

It is difficult as yet to state whether the reversal of sign observed at m = 55.51 is real or not, inasmuch as there is not enough experimental data, and the differences between the coefficients are too small. All that is apparent is that the derivatives are less affected by temperature at the higher concentrations.

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[*] I.E., up to a concentration that is considerably higher than the saturation concentration for the salts considered earlier.

[**] Considering the sum of the coordination numbers of solvation to be 17 in this case, i.e., 1 mol of water for the formation of H_3O^+ and 8 mols for the solvation of H_3O^+ and NO_3^-.

At $m = 55.5$, 1 mol of water is used for 1 mol of HNO_3, i.e., there can be no talk of solvation in the sense in which it was employed previously. This solution is equally a solution of the acid in water and of water in the acid.

The results of measurement in the $MgSO_4 \cdot 7H_2O$ system, cited in the 1st section of

TABLE 7

Temperature Coefficients of Integral Heats of Solution of KCl in Solutions of KNO_3 and of KNO_3 in Solutions of KCl, According to Holutta and Werner. Concentrations of the Dissolving Salts: KCl – 0.268 gram-equiv. per liter; KNO_3 – 0.178 gram-equiv per liter. Concentration of the Salt in the Solvent Given in Column 1. Temperatures: 20 and 25°.

Concentration of salt in the ready solvent, gram-equiv/liter	$\frac{d\Delta H_m}{dT}$ at 20-25° for KCl in a KNO_3 solution	$\frac{d\Delta H_m}{dT}$ at 20-25° for KNO_3 in a KCl solution	$\Delta H_{m_{20°}}$		$\Delta H_{m_{25°}}$	
			KCl in KNO_3 solutions	KNO_3 in KCl solutions	KCl in KNO_3 solutions	KNO_3 in KCl solutions
0.0	-34.0	-23.3	4445	8683	4275	8564
0.2	-33.0	-12.5	4240	8468	-	-
0.4	-27.7	- 4.8	4071	8343	-	-
0.6	-22.6	+ 1.2	3854	8118	-	-
1.0	-14.7	+ 8.8	3567	7643	3493	7637
1.5	- 9.0	-	3272	-	3227	-
2.0	-	+24.0	-	6744	-	6864
2.5	-	+27.2	-	4142	-	-

TABLE 8

Integral Heats of Solution and Their Temperature Coefficients for $HNO_3 - H_2O$, According to Mishchenko's Data (40°), the Tables of Bichowsky and Rossini (18°), and Forsyte's and Giaque's Data (25°)

Concentration, mols of acid per 1000 g H_2O	$\Delta H_{m_{18°}}$	$\Delta H_{m_{25°}}$	$\Delta H_{m_{40°}}$	$\frac{d\Delta H_m}{dT}_{18-25°}$	$\frac{d\Delta H_m}{dT}_{18-40°}$	$\frac{d\Delta H_m}{dT}_{25-40°}$
0	-7530	-7971	-8740	-63	-55	-51
0.139	-7445	-	-8218	-	-35	-
0.278	-7440	-	-8198	-	-34	-
0.555	-7444	-	-8165	-	-33	-
1.11	-7464	-	-8117	-	-30	-
2.22	-7502	-	-8055	-	-25	-
2.78	-7468	-	-8040	-	-26	-
5.55	-7320	-	-7690	-	-17	-
11.10	-6670	-	-6800	-	- 6	-
18.50	-5710	-5848	-5785	-20	- 3	+ 4
27.78	-4786	-	-4750	-	+ 2	-
55.51	-3290	-3239	-3200	+ 7	+ 4	+ 3

this paper, deserve separate consideration. The curves of ΔH_m and the temperature coefficients $d\Delta Hm/dT$ for this system are given in Table 9 and in Figs. 8 and 9, (the figures for 18° are taken from the tables published by Bichowsky and Rossini).

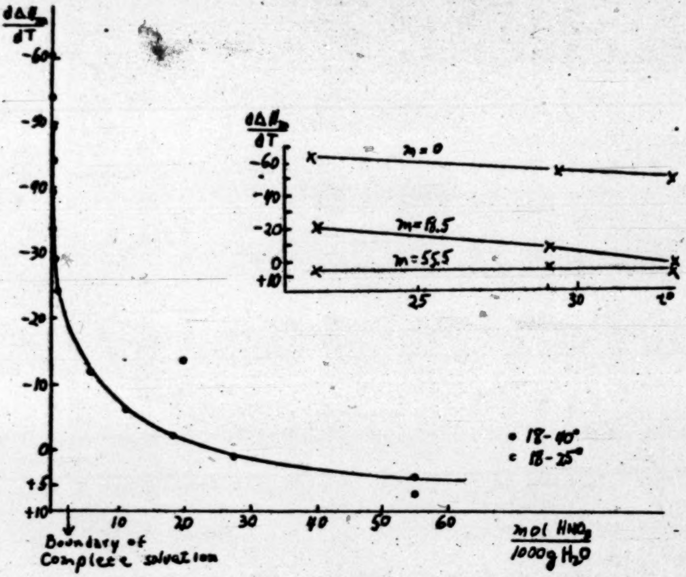


Fig. 7. Temperature coefficients of the heats of solution in the HNO_3 – H_2O system as a function of the concentration and the temperature.

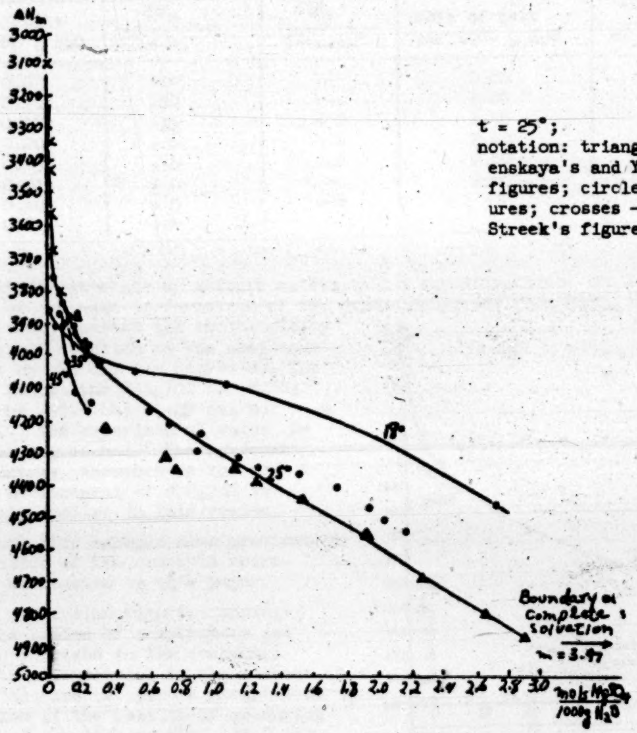
At first glance the behavior of this salt appears to be anomalous. The picture is not out of the ordinary for dilute solutions: the temperature coefficients are negative in the 18-25° range up to $\underline{m}$ = 0.31, i.e., ΔH_m becomes exothermic as the temperature is raised. The second derivatives are positive, as is usually the case. But above this concentration, $d\Delta H_m/dT$ becomes positive and attains fairly high positive values, all this occurring before the boundary of complete solvation is reached. Voskresenskaya and Yankovskaya [5] also drew attention to this phenomenon, endeavoring to explain it by the fact that the heat capacity of crystallohydrate water is lower than the heat capacity of "free" water. It seems to us that it is possible to give a more precise quantitative explanation for the effects observed.

When a crystallohydrate is dissolved, we must take into account not only the temperature coefficient of the heat of solution, but the temperature coefficient of the heat value of the reaction involving the formation of the crystallohydrate as well. We have computed the temperature coefficient of the heat of reaction of

$MgSO_4 + 7H_2O = MgSO_4 \cdot 7H_2O$. It is found to be 64 cal per degree-mol. Using the tabular data cited by Bichowsky and Rossini for the dissolution of anhydrous $MgSO_4$ (a typical Class I salt* with an exothermic dissolution effect, the exothermicity dropping as the concentration rises) and their data for the heats of formation of $MgSO_4 \cdot 7H_2O$ (cryst.) and $MgSO_4$ (cryst.) at 18°, we can calculate the heats of solution of $MgSO_4$ (anhydr.) at 25° and for a concentration, say, of m = 2.

This yields the following values, which we compare with our own values for $MgSO_4 \cdot 7H_2O$.

	t°	$\Delta H_m MgSO_4$	$\Delta H_m MgSO_4 \cdot 7H_2O$
m = 2	18	-20010	+ 4250
	25	-20148	+ 4560



t = 25°;
notation: triangles – Voskresenskaya's and Yankovskaya's figures; circles – our figures; crosses – Lange's and Streek's figures.

Fig. 8. Integral heats of solution of $MgSO_4 \cdot 7H_2O$.

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*Cf the Mischenko and Pronina classification [9].

It is apparent that we get a normal change of the heat of solution with temperature for the anhydrous salt, whereas the curve is reversed for the crystallohydrate; it is readily seen that the exothermicity of the heat of solution of the anhydrous salt rises only by -20 cal per degree mol, while the exothermicity of the heat of formation of the crystallohydrate rises by -64 cal per degree-mol, as we have pointed out. Hence, the temperature coefficient of the heat of solution of $MgSO_4 \cdot 7H_2O$ at m = 2 must be -20-(-64) = + 44 cal per degree-mol. The value found experimentally (Fig. 9) is +46 cal per degree-mol. The agreement may be termed excellent.

TABLE 9

Temperature Coefficients of the Heats of Solution of $MgSO_4 \cdot 7H_2O$ in Water, According to the Authors' Data (25°) and the Tables Published by Bichowsky and Rossini (18°)

Mols of salt per 1000 g H_2O	$\frac{d\Delta H_m}{dT_{18-25°}}$	$\frac{d\Delta H_m}{dT_{25-45°}}$	Mols of salt per 1000 g H_2O	$\frac{d\Delta H_m}{dT_{18-25°}}$
0.0	-14	-	0.80	+21
0.10	-20	-	1.00	+28
0.15	-13	+ 2	1.40	+36
0.20	- 6	+ 4	2.20	+49
0.25	- 4	+ 6	2.60	+53
0.31	± 0	-	2.80	+55
0.40	+ 5	+ 8		
0.60	+14	-		

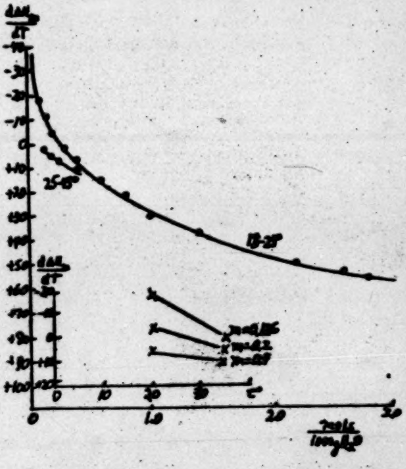

Fig. 9. Temperature coefficients of the integral heats of solution of $MgSO_4 \cdot 7H_2O$ in water.

A different state of affairs exists at low concentrations: the temperature coefficient of the heat of formation of the crystallohydrate from $MgSO_4$ and water remains constant, whereas the exothermicity of the heat of solution of the anhydrous salt rises by -93 cal per degree-mol for m = 0.1. Hence, the $d\Delta H_m/dT$ for $MgSO_4 \cdot 7H_2O$ must be -93-(-64) = -29 cal per degree-mol. The experimental value is -20 cal per degree-mol. The agreement is satisfactory, inasmuch as the precision of measurement of $d\Delta H_m/dT$ is considerably smaller in this region.

Thus, this example also provides a confirmation of the concepts underlying the discussion in this paper.

In connection with the analogy between the action of temperature and that of an increase in the concentration of the salt present in the solvent (cf Page 36), let us spend a moment upon a discussion of the results of measuring the heats of solution of $MgSO_4 \cdot 7H_2O$ in ready solutions of Na_2SO_4 cited in this paper. The integral heats of solution of $MgSO_4 \cdot 7H_2O$ as a function of the temperature and of the concentration of Na_2SO_4 in the "solvent" at a constant concentration $\underline{m}$ = 0.252 are shown in Fig. 10. The effects become less exothermic when the temperature is raised and when the concentration of Na_2SO_4 rises. To simplify the picture, which is obscured by the properties of the crystallohydrate, as pointed out above, we converted these figures into the heat of solution of anhydrous $MgSO_4$. The results are given in Table 10.

TABLE 10

Integral Heats of Solution of $MgSO_4$ (anhydr.) Up to a Concentration $\underline{m}$ = 0.252 Mol of Salt per 100 Mols H_2O, at Various Temperatures and Concentrations of Na_2SO_4 in the "Solvent"

Concentration Mols of salt per 100 mols of H_2O	$\Delta H_{m_{25^\circ}}$	$\Delta H_{m_{35^\circ}}$	$\Delta H_{m_{45^\circ}}$
0.00	-20873	-21495	-22146
5.60	-20868	–	–
8.16	-20846	–	–
11.49	-20843	–	–
14.16	-20835	–	–
14.36	–	-21306	-21938
23.26	-20808	–	–
27.85	-20772	-21228	-21693

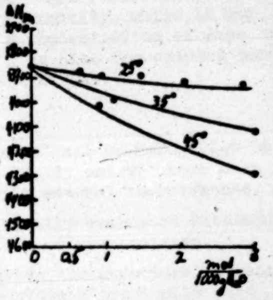

Fig. 10. Integral heats of solution of $MgSO_4 \cdot 7H_2O$ in Na_2SO_4 solutions.

As for the variation of ΔH_m with temperature when $MgSO_4 \cdot 7H_2O$ is dissolved in Na_2SO_4 solutions, all the considerations set forth above remain true. In Fig. 10, the exothermicity of ΔH_m drops as the temperature rises for $MgSO_4 \cdot 7H_2O$, whereas it rises for the anhydrous $MgSO_4$, as should be the case. The disruption of the structure of water by the action of Na_2SO_4 is not enough to mask the effect of temperature, which acts in the same direction. The high temperature coefficient of the heat of reaction in the formation of the crystallohydrate from water and the anhydrous salt produces reversed curves, as when no Na_2SO_4 is present.

The paper by Drucker [28] already referred to was the first to make a systematic study of the effect of outside electrolytes upon the ΔH_m. Drucker dissolved only the endothermic salt KCl, which is only slightly hydrated, in solutions of 28 electrolytes, however. He therefore noted only an increase in the exothermicity of dissolution. Voskresenskaya and Ponomareva [3] investigated a rather large number of combinations, dissolving a number of salts of various classes and KOH in solutions of a series of different electrolytes. Some of the combinations were investigated at several temperatures. As a result, instances were observed in which the exothermicity of dissolution decreased when the concentration of the salt forming part of the "solvent" was increased, alongside the more frequent rise in the exothermicity of dissolution.

In full conformity with all the notions developed by us above, this phenomenon is the more infrequent, the more highly hydrated the ions of the participants in the system and the less they disrupt the structure of the water. The dissolution of $MgSO_4 \cdot 7H_2O$ in Na_2SO_4 solutions investigated by us and described here is another instance of this type of system.

It is characteristic that in the systems studied by Voskresenskaya and Ponomareva exothermicity of dissolution in observed in the NaCl – $MgCl_2$ combination, but not in the KCl – $MgCl_2$ combination; in the NaCl – $CaCl_2$ combination, but not in the KCl – $CaCl_2$ combination (Drucker); i.e., the solvation series $Na^{\cdot} > K^{\cdot}$ and the series of the disrupting effect upon the structure of water, $K^{\cdot} > Na^{\cdot}$ are reflected here. The NaCl – $MgCl_2$ pair exhibits a systematic decrease in exothermicity, while in the NaCl – $CaCl_2$ it begins by rising, starting to drop only at a concentration of some 3 mols per 100 mols of water. Hence, the series $Mg^{\cdot\cdot} > Ca^{\cdot\cdot}$ is also represented here. The NaCl – $BaCl_2$ pair exhibits only an increase in the exothermicity.

SUMMARY

1. The integral heats of solution of KCl in water at 50° and of $MgSO_4 \cdot 7H_2O$ in water and in Na_2SO_4 solutions of varying concentrations at 25, 35 and 45° have been measured in a Vrevsky nonadiabatic calorimeter, provided with several improvements.

2. The authors' figures have been compared with critically evaluated literature data on the temperature coefficients of the heats of solution of electrolytes.

3. Conclusions have been reached concerning a change in the structure of water with temperature and concentration, which confirm the propositions previously laid down by the authors. It has been shown that the behavior of $MgSO_4 \cdot 7H_2O$ is not anomalous.

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THE PATTERNS OF SOLUBILITY CHANGE

IV. THE SOLUBILITY EQUATION FOR ISOTHERMS IN MULTICOMPONENT SYSTEMS

E. I. Akhumov and N. S. Spiro

1. INTRODUCTION

The present paper represents an elaboration of the notion set forth in our second [2] and third [3] papers dealing with the energy characteristics of solubility [1] for polytherms and isotherms in multicomponent systems; it deals with a solution of the problem of the nature of the solubility equation for isotherms in multicomponent systems.

2. FUNDAMENTAL FORMULAS

Assume we are dealing with a three-component aqueous salt system, say, with an identical anion R^{-1}:

$$M_rR_m - N_rR_n - H_2O \qquad (1)$$

where M^{+m} and N^{+n} are the cations.

Let us assume that under the specified conditions the components that constitute the solution do not form any chemical compound. Then the solubility isotherm will consist of two branches, corresponding to the solid phases M_rR_m and N_rR_n, which meet at the eutonic point.

As has been shown in our second paper [2], the magnitude of the derived equilibrium constants for the branches of the isotherm are calculated from the formulas:

$$\left.\begin{array}{lll} \text{Branch 1:} & (M_rR_m): & \bar{\varphi}_1 = \dfrac{m^m L_1^{m+1}}{C_1(mC_1 + nC_2)^m} \\ \text{Branch 2:} & (N_rR_n): & \bar{\varphi}_2 = \dfrac{n^n L_2^{n+1}}{C_2(mC_1 + nC_2)^n} \end{array}\right] , \qquad (2)$$

Where $\underline{L}_1$ and $\underline{L}_2$ are the separate solubilities, and $\underline{C}_1$ and $\underline{C}_2$ are the joint solubilities, computed in mols for a constant quantity of the solvent (water).

As has been shown in the third paper [3], for an isotherm the logarithm of the derived constant is proportional to the logarithm of the concentration of the component with which the solution is saturated, i.e.:

$$\left.\begin{array}{ll} \text{Branch 1:} & \ln \bar{\varphi}_1 = a_1 + b_1 \ln C_1 \\ \text{Branch 2:} & \ln \bar{\varphi}_2 = a_2 + b_2 \ln C_2 \end{array}\right] , \qquad (3)$$

where $\underline{a}$ and $\underline{b}$ are constants.

3. SOLUBILITY EQUATION FOR AN ISOTHERM

Eliminating $\overline{\varphi}_1$ and $\overline{\varphi}_2$, the magnitudes of the derived equilibrium constants, from Equations (2) and (3) we get:

$$\left.\begin{aligned} &\text{Branch 1:} && C_1^{b_1+1}(mC_1 + nC_2)^m = \frac{m^m L_1^{m+1}}{e^{a_1}} \\ &\text{Branch 2:} && C_2^{b_2+1}(mC_1 + nC_2)^n = \frac{n^n L_2^{n+1}}{e^{a_2}} \end{aligned}\right], \qquad (4)$$

where e is the basis of natural logarithms.

Equation (4) may be rewritten in the following form:

$$\left.\begin{aligned} &\text{Branch 1:} && C_1^{i_1}(mC_1 + nC_2) = K_1 \\ &\text{Branch 2:} && C_2^{i_2}(mC_1 + nC_2) = K_2 \end{aligned}\right], \qquad (5)$$

where i and K are new constants, namely:

$$\left.\begin{aligned} i_1 &= \frac{b_1 + 1}{m} \\ i_2 &= \frac{b_2 + 1}{n} \end{aligned}\right], \quad (6) \qquad \text{and} \qquad \left.\begin{aligned} K_1 &= me^{-\frac{a_1}{m}} L_1^{\frac{m+1}{m}} \\ K_2 &= ne^{-\frac{a_2}{n}} L_2^{\frac{n+1}{n}} \end{aligned}\right]. \qquad (7)$$

Formulas (4) and (5) are the equations of isothermal solubility in three-component systems.

As Equations (4) and (5) indicate, each branch of the solubility isotherm is determined by two constants: a and b for Equation (4), and i and K for Equation (5).

4. COMPUTING THE CONSTANTS a AND b

To compute the constants a and b in Equation (4), and hence, the constants i and K in Equation (5) we have to know two experimental values of the solubility, one for each branch of the solubility isotherm, inasmuch as it is assumed that the separate solubilities L_1 and L_2 are known. Moreover, it is enough to know only one value in order to compute the constants, if this value is the concentration of the solution at the eutonic point, lying on both branches of the isotherm.

We assume that the following experimental quantities are known in the three-component system under investigation:

$$\left.\begin{aligned} &\text{Separate solubilities} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots L_1,\ L_2 \\ &\text{Joint solubilities at the eutonic point} \ldots\ldots\ldots\ldots l_1,\ l_2 \end{aligned}\right]. \qquad (8)$$

The conditions for finding the constants a_1, b_1 and a_2, b_2 will then be:

$$\left.\begin{aligned} &\text{Branch 1:} && 1)\ \text{If}\ C_2 = 0, && \text{then}\ C_1 = L_1, \\ & && 2)\ \text{if}\ C_2 = l_2, && \text{then}\ C_1 = l_1; \\ &\text{Branch 1:} && 1)\ \text{if}\ C_1 = 0, && \text{then}\ C_2 = L_2, \\ & && 2)\ \text{if}\ C_1 = l_1, && \text{then}\ C_2 = l_2. \end{aligned}\right] \qquad (9)$$

Substituting Condition (9) in Equation (2), we get:

$$\left.\begin{array}{lll}\text{Branch 1:} & 1) & \bar{\varphi}_1 = \varphi_1 = 1,\\ & 2) & \bar{\varphi}_2 = \dfrac{m^m L_1^{m+1}}{\underline{l}_1(m\underline{l}_1 + n\underline{l}_2)^m} = \bar{\bar{\varphi}}_1;\\ \text{Branch 2:} & 1) & \bar{\varphi}_2 = \varphi_2 = 1,\\ & 2) & \bar{\varphi}_2 = \dfrac{n^n L_2^{n+1}}{\underline{l}_2(m\underline{l}_1 + n\underline{l}_2)^n} = \bar{\bar{\varphi}}_2.\end{array}\right] \qquad (10)$$

Substituting the values of $\bar{\varphi}_1$ and $\bar{\varphi}_2$ from Equation (10) in Equation (3) we get:

$$\left.\begin{array}{lll}\text{Branch 1:} & 1) & a_1 + b_1 \ln L_1 = 0,\\ & 2) & a_1 + b_1 \ln \underline{l}_1 = \ln \bar{\bar{\varphi}}_1;\\ \text{Branch 2:} & 1) & a_2 + b_2 \ln L_2 = 0,\\ & 2) & a_2 + b_2 \ln \underline{l}_2 = \ln \bar{\bar{\varphi}}_2.\end{array}\right] \qquad (11)$$

Solving the pairs of equations in (11) simultaneously yields the following results:

$$\left.\begin{array}{ll}\text{Branch 1:} & a_1 = \dfrac{\ln \bar{\bar{\varphi}}_1}{1 - \dfrac{\ln \underline{l}_1}{\ln L_1}},\\[3ex] & b_1 = \dfrac{\ln \bar{\bar{\varphi}}_1}{\ln \dfrac{\underline{l}_1}{L_1}};\\[3ex] \text{Branch 2:} & a_2 = \dfrac{\ln \bar{\bar{\varphi}}_2}{1 - \dfrac{\ln \underline{l}_2}{\ln L_2}},\\[3ex] & b_2 = \dfrac{\ln \bar{\bar{\varphi}}_2}{\ln \dfrac{\underline{l}_2}{L_2}}.\end{array}\right] \qquad (12)$$

We find the values of the coefficients $\underline{i}$ and $\underline{K}$ by inserting the values of the coefficients $\underline{a}$ and $\underline{b}$, found in Equation (12), in Equations (6) and (7).

5. SOLVING THE ISOTHERMAL SOLUBILITY EQUATION

The equations for the isothermal solubility (5) can be solved algebraically only when the equation is of no higher than the fourth degree.

The roots of the equation can be readily found by means of applied analysis, however, since the coefficients are computed numerically from the initial conditions. It is best to begin by using the graphical method, which yields an approximate result, to solve the solubility equation, and then to refine the result, say, by the method of successive approximations, until the desired degree of accuracy is attained [4,5].

6. USING THE ISOTHERMAL SOLUBILITY EQUATION

As an example of the application of the isothermal solubility equation, let us compute the solubilities in the ternary system NaCl – KCl – H_2O.

According to N.S.Kurnakov and N.A.Osokoreva [6], the solubility in the NaCl - KCl - H_2O system at 40° is defined by the following quantities (in mols per 1000 mols of H_2O):

	NaCl	KCl
Separate solubility	$L_1 = 112.60$	$L_2 = 97.74$
Joint solubility at the eutonic point . . .	$\underline{l}_1 = 90.82'$	$\underline{l}_2 = 47.74$

It is our problem to compute the solubility of KCl at 40° in solutions that are not saturated with NaCl, say (in mols per 1000 mols of H_2O):

	NaCl	KCl
Joint solubility along the branches	$C_1 = 51.02$	$C_2 = ?$

In the NaCl - KCl - H_2O system the coefficients $\underline{m} = \underline{n} = 1$.

The computation is performed as follows.

The derived equilibrium constant $\overset{=}{\varphi}_2$ for KCl at the eutonic point [from Equation (10)] is:

$$\overset{=}{\varphi}_2 = \frac{L_2^2}{\underline{l}_2(\underline{l}_1 + \underline{l}_2)} = \frac{97.74^2}{47.74(90.82 + 47.74)} = 1.4442.$$

The constants $\underline{a}_2$ and $\underline{b}_2$ for KCl are [from Equation (12)]:

$$a_2 = \frac{\ln \overset{=}{\varphi}_2}{1 - \dfrac{\ln \underline{l}_2}{\ln L_2}} = \frac{2.303 \log 1.4442}{1 - \dfrac{\ln 47.74}{\ln 97.74}} = 2.3508,$$

$$b_2 = \frac{\ln \overset{=}{\varphi}_2}{\ln \dfrac{\underline{l}_2}{L_2}} = \frac{\ln 1.4442}{\ln \dfrac{47.74}{97.74}} = - 0.51293$$

The constants $\underline{i}_2$ and $\underline{K}_2$ for KCl [from Equations (6) and (7)] are:

$$i_2 = b_2 + 1 = 1 - 0.51293 = 0.48707,$$

$$K_2 = e^{-a_2} L_2^2 = e^{-2.3508} \cdot 97.74^2 = 910.38.$$

Hence, Equation (5) for the solubility of KCl in solutions that are not saturated with NaCl takes on the form:

$$C_2^{0.48707} (C_1 + C_2) = 910.38.$$

Inasmuch as it has been assumed that $C_1 = 51.02$, we get: $C_2^{0.48707} = \dfrac{910.38}{51.02 + C_2}$.

To solve this equation we first find the approximate value of the root graphically; it is found to be

$$C_2 = 67.$$

Rewriting the equation in the following form: $C_2 = \dfrac{910.38}{C_2^{0.48707}} - 51.02,$

we solve it by the method of successive approximation:

First approximation: $C_2^{(1)} = \dfrac{910.38}{67^{0.48707}} - 51.02 = 66.41;$

Second approximation: $C_2^{(2)} = \dfrac{910.38}{66.41^{0.48707}} - 51.02 = 66.93;$

Third approximation: $C_2^{(3)} = \dfrac{910.38}{66.41^{0.48707}} - 51.02 = 66.43.$

Fourth approximation: $C_2^{(4)} = \dfrac{910.38}{66.43^{0.48707}} - 51.02 = 66.90$

As the calculations show, the root of the equation lies within the limits

$$C_2^{(4)} > C_2 > C_2^{(3)}$$

Since the method of successive approximations converges slowly, but uniformly, from both limits, we may assume that the value of the root is the arithmetical mean of the limiting values, i.e.:

$$C_2 = \frac{66.43 - 66.90}{2} = 66.66.$$

According to N.S.Kurnakov and N.A.Osokoreva [6], the solubility of KCl is 66.88. The discrepancy between the calculated and the experimental solubility values is:

$$100\,\frac{66.88 - 66.66}{66.88} = 0.33\%,$$

which is quite satisfactory.

SUMMARY

1. The solubility equation for isotherms in multicomponent systems has been derived from the relationships for the derived equilibrium constant.

2. One of the possible solutions of the isothermal solubility equations is given.

3. The use of the isothermal solubility equation in practical computations is illustrated by the example of the NaCl - KCl - H_2O system.

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*See CB translation p. 15 ff.

**See CB translation p. 205 ff.

THE PATTERNS OF SOLUBILITY CHANGE

V. RAOULT'S LAW

E. I. Akhumov and N. S. Spiro

1. Introduction

The feasibility of providing an energy characterization of the processes occurring in equilibrium systems and the solution of the behavior patterns of concentrated solutions of strong electrolytes are closely related to deviations of the ideal from the real laws over a wide range of concentrations [1,2,3,4].

The present paper, which deals with Raoult's Law, shows that concentrated solutions of strong electrolytes have their own regular patterns of behavior.

2. Raoult's Law

According to Raoult's Law, for ideal solutions the pressure of the saturated vapor above the solution π and that above the pure solvent P_0 in a binary system are interrelated by the following equation at constant temperature:

$$\pi = P_0 N, \tag{1}$$

where $\underline{N}$ is the mol fraction of the solvent in the solution.

It follows from Equation (1) that:

$$P_0 - \pi = P_0(1 - N), \tag{2}$$

i.e., the reduction in the pressure of the saturated vapor of the solvent above the solution is proportional to the mole fraction of the solute.

If the composition of the solution is determined by the number of mols of the non-volatile solute $\underline{C}$ per a constant number of mols (1000 mols) of the solvent:

$$N = \frac{1000}{1000 + C}, \tag{3}$$

it follows from Equations (2) and (3) that:

$$P_0 - \pi = P_0 \frac{C}{1000 + C}. \tag{4}$$

We reduce Equation (4) to the form:

$$C = r(P_0 - \pi), \tag{5}$$

where $\underline{r}$, Rauolt's coefficient, is:

$$r = \frac{C}{P_0 - \pi}. \tag{6}$$

As Equation (6) indicates, the Raoult coefficient shows how many molecules of a substance must be added to a solvent to produce a reduction in the saturated vapor pressure of the solvent above an ideal solution per unit pressure.

3. The Isothermal Change in the Values of the Raoult Coefficients for Unsaturated and Saturated Solutions

It follows from Equations (4) and (5) that:

$$r = \frac{1000 + C}{P_0}, \tag{7}$$

i.e., at constant temperature, the Raoult coefficient should increase in proportion to the concentration of the solute for ideal solutions.

In that case, if the concentration of the solute is low compared to that of the solvent:

$$C \ll 1000 \tag{8}$$

it follows from Equation (7) that:

$$\lim_{C \to 0} r = \frac{1000}{P_0}, \tag{9}$$

i.e., the value of the Raoult's coefficient for ideal solutions approaches the limiting value in an infinitely diluted solution.

Thus, in the graphic interpretation of Equation (7), the relationship between r and C must be represented by a straight line, with r increasing with increasing values of C.

TABLE 1

Values of the Raoult Coefficient for Solutions in the $NaNO_3 - H_2O$ System at 85° [5]

C, mols per 1000 mols of H_2O	$\frac{100(P_0-\pi)}{MP_0}$	π mm Hg	$P_0-\pi$ mm Hg	r
18.02	3.40	418.9	14.7	1.222
54.05	3.10	393.3	40.3	1.341
90.10	2.93	370.1	63.5	1.418
126.1	2.79	348.9	84.7	1.489
180.2	2.60	320.8	112.8	1.598
252.3	2.40	287.9	145.7	1.732

For concentrated solutions, the experimental data do not confirm the correctness of the corollaries of Equations (7) and (9).

Thus, for solutions at 85° in the $NaNO_3 - H_2O$ system [5], the value of the Raoult coefficient rises linearly with an increase in the concentration of the solution, in accordance with Equation (7) (Table 1, Fig. 1).

For solutions of the $Na_2SO_4 - H_2O$ system at 50° [6], the Raoult coefficient is approximately constant (Table 2).

For solutions in the $NaCl - H_2O$ system at 20° [7], the value of the Raoult coefficient drops linearly as the concentration rises (Table 3, Fig. 2).

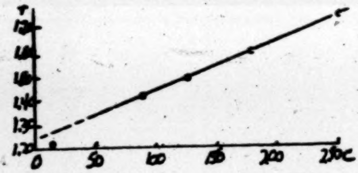

Fig. 1. Change in r in the $NaNO_3 - H_2O$ system at 85°.

Thus, the variation of the Raoult coefficient with the concentration in concentrated solutions is expressed by the following equation:

$$r = r_0 + \rho C, \tag{10}$$

where r_o is the extrapolated value of the Raoult coefficient in an infinitely diluted solution, and ρ is a coefficient that varies with the nature of the substance and the thermodynamic conditions selected.

It follows from an explanation of the change in the Raoult coefficient under isothermal conditions that the coefficient ρ remains constant in the interval:

$$0 < C \leqslant L \qquad (11)$$

where L is the separate solubility.

There are three possible types of change in the values of the Raoult coefficient, depending upon the magnitude of the coefficient ρ .

1) At $\rho > 0$, the Raoult coefficient rises with increasing concentration;

2) At $\rho = 0$, $r = r_o$, i.e., the Raoult coefficient is constant throughout the range of concentration changes.

3) At $\rho < 0$, the Raoult coefficient falls as the concentration rises.

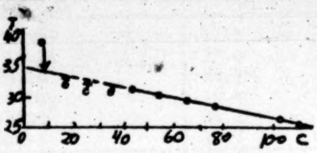

Fig. 2. Change in r in the NaCl - H_2O System at 20°

It should be noted that the behavior pattern represented by Equation (10) is also confirmed by several other experimental figures in the region of concentrated solutions, including saturated solutions.

TABLE 2

Value of the Raoult Coefficient for Solutions in the $Na_2SO_4 - H_2O$ System at 50° [6]
$P_o = 92.5$ mm Hg

C, mols per 1000 mols of H_2O	π mm Hg	$P_o - \pi$ mm Hg	r	Remarks
6.677	91.2	1.3	5.137	Unsaturated solution
14.09	89.8	2.7	5.220	
22.39	88.2	4.3	5.206	
31.71	86.4	6.1	5.199	
42.30	84.4	8.1	5.222	
54.37	81.7	10.8	5.034	
61.95	80.4	12.1	5.121	Saturated solution

4. Polythermal Change of the Value of the Raoult Coefficient for Unsaturated Solutions

Let us now consider that change in the Raoult coefficient with temperature for unsaturated solutions of constant concentration in binary systems.

It follows from Equation (6) that the Raoult coefficient is determined by the ratio of the solution concentration C to the difference in the saturated vapor pressures above the pure solvent P_o and above the solution π . In solutions of constant concentration, the quantities P_o and π vary with temperature exponentially [1]:

TABLE 3 $P_0 = 17.5$ mm Hg

Value of the Raoult Coefficient for Solutions in the NaCl – H_2O System at 20° [7]

C, mols per 1000 mols of H_2O	π mm Hg	$P_0 - \pi$ mm Hg	r	Remarks
7.903	17.3	0.2	39.52	Unsaturated solution
1.623	17.0	0.5	32.45	
25.00	16.7	0.8	31.25	
34.26	16.4	1.1	31.14	
44.03	16.1	1.4	31.46	
54.41	15.7	1.8	30.21	
65.37	15.3	2.2	29.72	
77.05	14.8	2.7	28.54	
89.50	14.2	3.5	25.57	
102.8	13.6	3.9	26.34	
110.6	13.2	4.3	25.71	Saturated solution

TABLE 4

Value of the Raoult Coefficient for Unsaturated Solutions in the NaCl – H_2O System [7]

t	$\frac{1}{t}$	P_0 mm Hg	π mm Hg	$P_0 - \pi$ mm HG	r	log r
			C = 34.24 mols per 1000 mols of H_2O			
0°	0.003663	4.6	4.3	0.3	114.1	2.0574
20	0.003413	17.5	16.4	1.1	31.13	1.4931
40	0.003195	55.3	51.7	3.6	9.510	0.9782
60	0.003003	149.5	139.7	9.8	3.493	0.5433
80	0.002833	355	332	23	1.489	0.1728
100	0.002681	760	710	50	0.6847	-0.1645
110	0.002611	1075	1003	72	0.4755	-0.3228
			C = 77.06 mols per 1000 mols of H_2O			
0°	0.003663	4.6	3.8	0.8	96.34	1.9837
20	0.003413	17.5	14.8	2.7	28.64	1.4554
40	0.003195	55.3	46.6	8.7	8.857	0.9473
60	0.003003	149.5	126.0	23.5	3.278	0.5157
80	0.002833	355.5	300.5	55.0	1.401	0.1464
100	0.002681	760	643	117	0.6586	-0.1814
110	0.002611	1075	911	164	0.4699	-0.3280

$$P_0 = \exp\left(\frac{A_{P_0}}{T} + B_{P_0}\right) \tag{12}$$

$$\pi = \exp\left(\frac{a_\pi}{T} + b_\pi\right), \tag{13}$$

where A_{P_0}, B_{P_0} a_π, and b_π are constants, and T is the absolute temperature.

If in Formula (6) we insert the values of P_0 and π as given in Equations (12) and (13) and assume that $\underline{C}$ = const., the theory of series yields the equation:

$$r = \exp\left(\frac{a_r}{T} + b_r\right), \qquad (14)$$

where $\underline{a_r}$ and $\underline{b_r}$ are constants.

Equation (14) shows that in unsaturated solutions, the changes in the logarithm of the Raoult coefficient is proportional to the reciprocal of the temperature. Experimental data confirm the correctness of Equation (14).

The relationship expressed by Equation (14) actually holds good for 10% and 20% aqueous solutions of sodium chloride [7] throughout the temperature range 0 - 110° (Table 4, Fig. 3).

The function expressed by Equation (14) is likewise confirmed for aqueous solutions of sodium nitrate, in concentrations of 80 and 100 g per 100 g of H_2O [8], in the temperature range 0-125° (Table 5, Fig. 4).

TABLE 5

Value of the Raoult Coefficient for Unsaturated and Saturated Solutions in the $NaNO_3$ – H_2O System [8]

t	$\frac{1}{T}$	C, mols per 1000 mols of H_2O	P_0, mm Hg	π mm Hg	$P_0 - \pi$ mm Hg	r	log r	Remarks
0°	0.003663	169.6	4.58	3.64	0.94	180.4	2.2563	Supersaturated solution
25	0.003356	169.6	23.76	18.29	5.47	31.00	1.4914	Unsaturated solution
50	0.003096	169.6	92.54	70.25	22.29	7.608	0.8813	
75	0.002874	169.6	289.3	217.8	71.5	2.372	0.3751	
100	0.002681	169.6	760.0	568.2	191.8	0.8843	-0.0534	
125	0.002513	169.6	1741	1294	447	0.3794	-0.4209	
25	0.003356	211.9	23.76	17.29	6.47	32.76	1.5154	Supersaturated solution
50	0.003096	211.9	92.5	66.1	26.4	8.030	0.9047	Unsaturated solution
75	0.002874	211.9	289.3	204.3	85.0	2.494	0.3969	
100	0.002681	211.9	760.0	531.6	228.4	0.9497	-0.0324	
125	0.002513	211.9	1741	1209	532	0.3985	-0.3996	
0	0.003663	154.7	4.58	3.70	0.88	175.8	2.2451	Saturated solution
10	0.003534	170.6	9.21	7.20	2.01	84.89	1.9289	
20	0.003413	186.9	17.54	13.25	4.29	43.58	1.6393	
30	0.003300	203.9	31.82	23.27	8.55	23.85	1.3775	
40	0.003195	222.2	55.32	39.13	16.19	13.73	1.1375	
60	0.003003	262.8	149.4	98.6	50.8	5.174	0.7138	
80	0.002833	313.7	355.1	216.1	139.0	2.257	0.3536	
100	0.002681	373.1	760.0	422.9	337.1	1.107	0.0441	
120	0.002545	446.4	1489.2	748.5	740.7	0.6027	-0.2199	
125	0.002513	467.0	1741.0	851.6	889.4	0.5250	-0.2798	

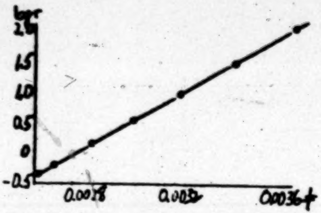

Fig. 3. Change in r with temperature in the NaCl – H_2O system (34.24 mols per 1000 mols H_2O).

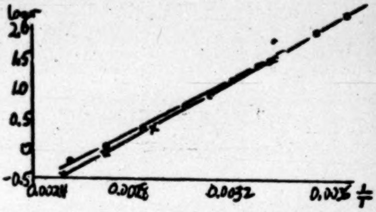

Fig. 4. Change in r with temperature in the $NaNO_3$ – H_2O system.

5. Polythermal Change in the Values of the Raoult Coefficient for Saturated Solutions

For saturated solutions the Raoult coefficient is:

$$r = \frac{L}{P_0 - P_1}, \tag{15}$$

where L is the separate solubility (concentration of the saturated solution); P_0 is the saturated vapor pressure above the pure solvent; and P_1 is the saturated vapor pressure above the saturated solution.

TABLE 6

Value of the Raoult Coefficient for Saturated Solutions in the $C_{12}H_{22}O_{11}$ – H_2O System [9]

t	$\frac{1}{T}$	L mols per 1000 mols of H_2O	P_0 mm HG	P_1 mm Hg	$P_0 - P_1$ mm Hg	r	log r
0°	0.003660	94.77	4.58	4.04	0.54	175.5	2.2443
10	0.003531	100.7	9.21	8.03	1.18	85.37	1.9313
20	0.003411	107.8	17.5	15.1	2.4	44.92	1.6525
30	0.003298	116.1	31.8	26.9	4.9	23.69	1.3745
40	0.003193	125.9	55.3	45.8	9.5	13.25	1.1224
50	0.003094	137.7	92.5	74.6	17.9	7.693	0.8861
60	0.003001	151.9	149.4	116.5	32.9	4.618	0.6645
70	0.002914	169.3	234	174	60.0	2.823	0.4507

The quantities entering into Equation (15) vary exponentially with the temperature [1]:

$$L = \exp\left(\frac{A_L}{T} + B\right), \tag{16}$$

$$P_1 = \exp\left(\frac{A_{P_1}}{T} + B_{P_1}\right). \tag{17}$$

TABLE 7

Value of the Raoult Coefficient for Saturated Solutions in the $KCl - H_2O$ System [10]

t	$\frac{1}{T}$	L mols per 1000 mols of H_2O	P_0 mm Hg	P_1 mm Hg	$P_0 - P_1$ mm Hg	r	log r
20°	0.003413	82.17	17.5	15.5	2.0	41.09	1.6137
25	0.003356	85.78	23.8	20.5	3.3	25.95	1.4149
30	0.003300	89.41	31.8	26.9	4.9	18.25	1.2612
40	0.003195	96.68	55.3	45.8	9.5	10.17	1.0076
50	0.003096	102.9	92.5	74.8	17.7	5.816	0.7646
100	0.002681	135.6	760.0	567.8	192.2	0.7055	-0.1515

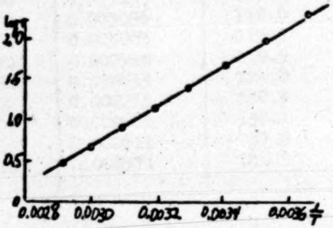

Fig. 5. Change in r with temperature for saturated solutions in the $C_{12}H_{22}O_{11} - H_2O$ system.

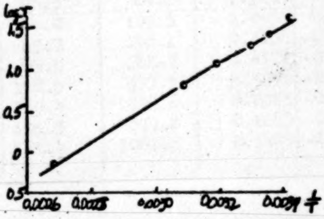

Fig. 6. Change in r with temperature for saturated solutions in the $KCl - H_2O$ system.

Substituting the values of P_0, P_1, and L from Equations (12), (16), and (17) in Equation (15), we use the theory of series to obtain:

$$r = \exp\left(\frac{A_r}{T} + B_r\right), \qquad (18)$$

where A_r and B_r are constants.

Equation (18) indicates that the change in the logarithm of the Raoult coefficient is proportional to the reciprocal of the absolute temperature for a saturated solution. The experimental data confirm the correctness of Equation (18).

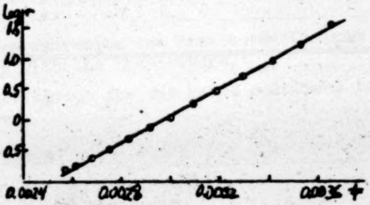

Fig. 7. Change in r with temperature for saturated solutions in the $MgCl_2 - H_2O$ system.

The following saturated solutions in binary system are cited below as examples: $C_{12}H_{22}O_{11} - H_2O$ in the temperature range 0 to 70° [9] (Table 6, Fig. 5); $KCl - H_2O$ in the temperature range 20 to 100° [10] (Table 7, Fig. 6); $MgCl_2 - H_2O$ in the temperature range 0-116° [10] (Table 8, Fig. 7); and $NaNO_3 - H_2O$ in the temperature range 0-125° [8] (Table 5, Fig. 4).

TABLE 8

Value of the Raoult Coefficient for Saturated Solutions in the $MgCl_2 - H_2O$ System [11]

t	$\frac{1}{T}$	L mols per 1000 mols of H_2O	P_0 mm Hg	P_1 mm Hg	$P_0 - P_1$ mm Hg	r	log r
0°	0.003663	98.9	4.58	1.56	3.02	32.78	1.5154
10	0.003534	101.3	9.21	3.08	6.13	16.51	1.2178
20	0.003413	103.5	17.54	5.77	11.77	8.790	0.9440
30	0.003300	106.1	31.8	10.3	21.5	4.938	0.6935
40	0.003195	109.0	55.3	17.4	37.9	2.876	0.4587
50	0.003096	112.0	92.5	28.3	64.2	1.745	0.2417
60	0.003003	115.5	149.5	44.0	105.5	1.095	0.0396
70	0.002915	119.9	233.8	65.7	168.1	0.7136	-0.1466
80	0.002833	124.8	355.5	93.8	261.7	0.4772	-0.3213
90	0.002755	130.9	525.8	128.5	397.3	0.3296	-0.4821
100	0.002681	138.1	760.0	165.4	594.6	0.2323	-0.6340
110	0.002611	147.9	1074.5	195.3	879.2	0.1683	-0.7740
116	0.002571	158.5	1268.0	186.4	1081.6	0.1465	-0.8341

SUMMARY

1. The concept of the Raoult Coefficient has been introduced, which determines the number of molecules of the solute that causes a reduction in the saturated vapor pressure of the solvent above the solution per unit pressure.

2. It has been shown that at constant temperature the Raoult coefficient always varies linearly with the concentration over a wide range of solution concentrations, up to saturation. The slope of the line with respect to the axis of concentrations depends on the chemical nature of the solute.

3. It has been proven that at constant concentration the Raoult coefficient for unsaturated solutions varies exponentially with the temperature.

4. It has been proven that the Raoult coefficient for saturated solutions likewise varies exponentially with the temperature.

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*See CB translation p. 15 ff.

**See CB translation p. 205 ff.

DETERMINATION OF THE ENERGY EFFECTS OF DILUTING HIGH POLYMER SOLUTIONS BY A DILATOMETRIC METHOD

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For the thermodynamic characterization of high-polymer solutions, experimental data are available on the changes occurring in two of the three variables in the equation $\Delta F = \Delta H - T\Delta S$, when these solutions are diluted. The change in the heat content ΔH is usually determined calorimetrically [1] or indirectly from the temperature coefficient of the osmotic pressure [2]. But neither of these methods provides sufficiently accurate results, and sometimes they do not even allow of a confident evaluation of the presence of any thermal effect at all or of its sign. Both of these methods are quite useless for highly diluted solutions. That is why we have endeavored to employ a method hitherto unused for this purpose - the dilatometric method - to measure the energy effects of dilution.

It is a matter of course that the change in the aggregate volume of a system during various processes (swelling, dissolution, dilution) must correspond in one way or another to the change in the system's energy, i.e., the heat value, that takes place therewith. Katz once showed that the ratio of the volume to the thermal effect during swelling is a constant for a given system, ranging from $10 \cdot 10^{-4}$ to $60 \cdot 10^{-4}$ for different systems [3]. Thus, the change in volume may serve not only as a qualitative index, but also as an approximate quantitative index of the energy change in the process. In any event, the nature of the change in the energy effect during the process may be reliably studied by means of this method.

Research Methods and Objectives

One of the present authors has suggested a device for determining small changes in volume that occur when certain liquids are mixed together, which makes it possible to study the processes of solvation and desolvation of high-polymers when the composition of the solvent is changed [4].

The dilatometer used by us to study the effects of swelling (Fig. 1) was based on the same principle of connecting vessels separated by a mercury seal. The dilatometer used for dilution was even simpler: it does not have the branch tube D shown in Fig. 1, through which a dry substance is introduced into compartment B during the investigation of swelling, after which the tube is sealed off; nor does it have the conical portion E, which keeps that substance within compartment B. The dilatometer is filled through the capillaries K_1 and K_2, which also serve as measuring capillaries. (Mercury is introduced into the connecting elbow C through one of the capillaries; it serves to separate the solvent from the diluting solution. The solution is introduced into compartment B through the capillary K_2, and the solvent into compartment A through capillary K_1) The funnel-shaped mouths of the capillaries are closed by stoppers after the device has been filled, and the dilatometer is placed in a large water thermostat, the temperature of which is kept constant within ± 0.002°. Once the temperature of the liquid in the dilatometer is found to be constant which is indicated by the constant levels in the capillaries, the two meniscus heights are read off. Then the device is withdrawn from the thermostat, and the two liquids are mixed together by repeatedly pouring the mercury from one elbow into the other, while lightly shaking the device. Then the device is put into the thermostat again, and after constant temperature has been reached, the two meniscus heights in the capillaries are read off again (during mixing care must be taken that the levels of the liquid do not rise above the top of the capillaries, which practically eliminates evaporation). Control tests have shown that analogous operations performed with the same liquid in both reservoirs of the device do not cause any change in its overall volume (within the limits corresponding to a temperature fluctuation of ± 0.002°).

TABLE 1

Dilatometer	Reservoir volume, ml		Capillary radius mm	
	A	B	K_1	K_2
1	200-250	20-25	0.0557	0.0645
2	250-300	3-15	0.0531	0.0519
3	200-240	200-240	0.0577	0.0580
4	225-250	225-250	0.0550	0.0560

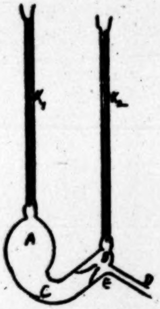

Fig. 1. Dilatometer for investigating the volumetric effects of swelling.

In order to be able to measure the ratios between the quantities of the diluting solution and the solvent over a wider range than is possible with a single device, we used several instruments, differing in the volume of their elbows. They are described in Table 1.

The following solutions were used in our research: a) nitrocellulose ([η] = 1.60) in acetone; b) the same nitrocellulose in the ether of ethyl acetate; c) the ether of cellulose and benzylalcohol in benzene; d) the ether of cellulose and ethyl alcohol ([η] = 1.80, ethoxy groups = 48.4%) in benzene; the ether of cellulose and ethyl alcohol in ethyl acetate; f) citrus pectin in water; g) polystrene in benzene; and h) nitrocellulose in dioxane.

EXPERIMENTAL

The results of our determinations of the volumetric effects of dilution for the systems: nitrocellulose – acetone are listed in Table 2. Column 9 of this table shows the change in the total volume of the liquid in the dilatometer (actual test results). These figures, despite their small size, correspond to a temperature change of 0.028-0.043° (calculated from the temperature coefficients measured for each device), i.e.,

TABLE 2

Volumetric Effect of Diluting Solutions of Nitrocellulose ($\eta = 1.60$) in Acetone

Contractometer No.	Weight, g		Concentration, %		Weight of nitrocellulose, g	Δh, cm Capillary		Δv ml	$\Delta v/m$ ml/g	Q computed, cal/g
	Acetone	Solution	Initial	Final		Left	Right			
1	199.0	21.1	10.0	1.0	2.11	0.57	0	0.0054	0.0023	0.34
1	192.3	22.9	10.0	1.0	2.29	0.72	0	0.0068	0.0029	0.42
4	168.2	168.2	2.0	1.0	3.35	0.56	0	0.0052	0.0016	0.23
2	247.0	7.05	15.0	0.5	1.14	0.60	0	0.0053	0.0046	0.68
3	185.7	185.7	1.0	0.5	1.85	0.32	0	0.0034	0.0018	0.26
2	232.0	11.25	10.0	0.4	1.12	0.60	0	0.0066	0.0059	0.89
2	235.0	20.07	5.0	0.4	1.00	0.44	0	0.0039	0.0039	0.57
3	170.0	170.0	0.8	0.4	1.36	0	0	0.0000	0.0000	0.00
4	181.7	181.7	0.6	0.3	1.09	0.37	0	0.0040	0.0037	0.53
4	190.0	190.0	0.5	0.25	0.95	0.70	0.68	0.0170	0.0179	2.63
4	177.0	177.0	0.53	0.26	0.93	1.3	0	0.0151	0.0163	2.39
2	250.0	3.2	15.0	0.19	0.48	1.6	0	0.0158	0.0330	4.88
4	188.0	188.0	0.4	0.2	0.75	1.72	0	0.0187	0.0250	3.68
3	177.2	177.2	0.4	0.2	0.35	0	1.77	0.0187	0.0238	3.50
4	167.5	167.5	0.2	0.1	0.33	0.38	0	0.0036	0.0117	1.72
4	171.2	171.2	0.1	0.05	0.17	0.1	0	0.0009	0.0056	0.14
3	180.0	180.0	0.05	0.025	0.09	0	0	0.0000	0.0000	0

they are 10 to 20 times as great as the volumetric effects that might be caused by a fluctuation of the temperature of ± 0.002°. In Column 10 the magnitude of the volumetric effect of dilution has been recomputed in terms of 1 g of dry nitrocellulose.

These results disclose that the volumetric effects vary with the degree of dilution. This variation is shown graphically in Fig. 2. The marked bend in the curve is located in the concentration region of 0.3-0.2%; the volumetric effects are represented numerically as 0.001-0.006 ml per gram when 10 to 15% nitrocellulose solutions are diluted to concentrations above 0.3%, whereas the effects are 0.010-0.030 ml per gram for dilutions from 0.3% to 0.25-0.10%, the total volumetric effect of dilution from 10% to 0.025% amounting to about 0.050 ml per gram.

To get an idea of the magnitude of these quantities, we determined the volumetric effects of dissolving the same nitrocellulose; this was done by introducing dry nitrocellulose into elbow B̲ of the dilatometer through the branch tube D̲, after which benzene was introduced through capillary K_2, benzene being chosen as an indifferent liquid because of the slight volumetric effects of mixing it with acetone. Acetone was introduced into elbow A̲. The two liquids were mixed together by pouring them from one reservoir into the other; this was accompanied by dissolution of the nitrocellulose. The volumetric effect of dissolution was determined by the difference between this effect and that in the control test, in which the corresponding quantities of benzene and acetone were mixed together. The results (Table 3) show that if the volumetric effect of dilution from 0.5 to 0.05% (which Table 2 indicates totals about 0.04 ml per gram) is added to the resulting figure of 0.1167 ml per gram, that the integral volumetric effect of dissolution is represented by a figure of the order of 0.16 ml per gram. The effect of dilution from 10% to 0.4% does not represent more than 5% of the integral effect of dissolution, whereas the volumetric effect of dilution from 0.3% to 0.05% is as much as 25% of the integral figure.

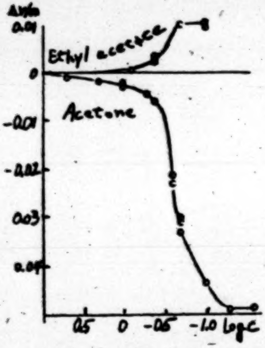

Fig. 2. Volumetric effects of diluting solutions of nitrocellulose with acetone and ethyl acetate.

TABLE 3

Volumetric and Thermal Effects of Dissolving Nitrocellulose in Acetone and the Ether of Cellulose and Benzyl Alcohol in Benzene

System	Δv/m ml/g	Q(experi.) in cal/g	$\frac{\Delta v/m}{Q}$
Nitrocellulose in acetone	-0.1167	17.0	$68\cdot10^{-4}$
Ether of cellulose and benzyl alcohol in benzene...	-0.0123	2.5	$48\cdot10^{-4}$

A similar, though not quite identical, ratio must obviously exist between the thermal effects of dissolution and dilution.

The thermal effect of dissolving nitrocellulose in acetone up to a concentration of about 2% was measured calorimetrically; our value for the integral heat of swelling, 17.0 cal per gram, is close to the value found for the same system by other authors: Kargin (18 cal per gram), and Nakachima, (21 cal per gram) [1].

Comparing the thermal and volumetric effects of dissolution, we get: $\frac{\Delta v/m}{Q} = \frac{0.116}{17.0} = 68\cdot10^{-4}$. This ratio may be used for an approximate calculation of the values of the thermal effects of dilution in the concentration ranges investigated by us. These values are listed in Column 11 of Table 2.

Thus, the curve showing the variation of the thermal effects of dissolution with the concentration, like the curve of volumetric effects, has two sharp bends; an appreciable contraction of the system, accompanied by the evolution of heat, of the order of 18 cal, occurs in the region of swelling; the effect of dilution is relatively insignificant down to a concentration of 0.3%; and lastly, a fairly large energy effect occurs again at still higher dilutions.

Table 4 lists the data obtained for other systems. This table shows that the volumetric effects of diluting nitrocellulose in ethyl acetate are positive, their absolute magnitude being much smaller than the negative volumetric effects of diluting nitrocellulose in acetone, even though the bend in the curve is located in the same concentration region, 0.40-0.20%, as for acetone solutions of the same nitrocellulose, as is seen in Fig. 2.

The effects of diluting the ether of cellulose and ethyl alcohol (Table 4, Fig. 3) in benzene and in ethyl acetate are positive. In benzene the marked bend in the $\frac{\Delta v}{m}$ - c curve lies in the concentration region of 0.5-0.2%; dilution from 5% to 0.5% is accompanied by a change in volume of 0.0014 ml per gram, whereas dilution from 0.4% to 0.2% involves a volumetric effect of 0.0032 ml per gram; diluting the solutions below 0.2% does not cause any change in volume.

TABLE 4

Volumetric Effects of Dilution

Nitrocellulose in ethyl acetate

Concentration, % Initial	Concentration, % Final	$\frac{\Delta v}{m}$, ml/g
4.0	0.4	+ 0.0033
4.0	0.2	+ 0.0100
4.0	0.1	+ 0.0096
0.8	0.4	+ 0.0018
0.4	0.2	+ 0.0067
0.2	0.1	0.0000

Ether of cellulose and benzyl alcohol in benzene

Concentration, % Initial	Concentration, % Final	$\frac{\Delta v}{m}$, ml/g	Q, computed cal per g
10.0	1.2	0	0
10	0.2	-0.0074	1.48
5	0.3	-0.0032	0.66
5	0.5	-0.0013	0.27
2	0.04	-0.0090	1.87
0.5	0.25	-0.0070	1.45

Ether of cellulose and ethyl alcohol in ethyl acetate

Concentration, % Initial	Concentration, % Final	$\frac{\Delta v}{m}$, ml/g
10.0	1.0	+ 0.0015
1.0	0.5	+ 0.0008
0.5	0.25	+ 0.0020
0.4	0.2	+ 0.0013
0.25	0.12	+ 0.0038
0.25	0.10	+ 0.0049
1.0	0.1	+ 0.0060
0.1	0.05	+ 0.00078

Ether of cellulose and ethyl alcohol in benzene

Concentration, % Initial	Concentration, % Final	$\frac{\Delta v}{m}$, ml/g
5.0	0.5	+0.0014
0.4	0.2	+0.0032
5.0	0.1	+0.0071
0.2	0.1	+0.0000
0.1	0.05	+0.0000

In ethyl acetate, the increase in the volumetric effects of dilution sets in at a concentration of 0.4%; dilution of a 1% solution by half causes an increase in volume by 0.0008 ml per gram, whereas diluting a 0.5% solution by half produces an increase of 0.0020 ml per gram, and diluting a 0.1% solution by half produces an increase of 0.0078 ml per gram. For this system we did not find a region of low concentration in which dilution is not accompanied by a change in volume; apparently, this may take place at concentrations below 0.05%, which cannot be investigated by the method we employed.

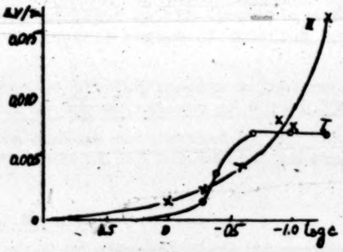

Fig. 3. Volumetric effects of diluting a solution of the ether of ethyl alcohol and cellulose with benzene (I) and ethyl acetate (II).

In contrast to the system of the ether of cellulose and ethyl alcohol - benzene, the volumetric effects of diluting the ether of cellulose in benzyl alcohol are negative (Table 4, Fig. 4). The bend in the $\frac{\Delta v}{m}$ - c curve lies in the concentration range of 0.5-0.2%. We also measured the volumetric and thermal effects of dissolution for this system. To determine the volumetric effect we placed a weighed amount of the ether of cellulose in benzyl alcohol and water in the right-hand elbow of the dilatometer, and a certain quantity of benzene (about 200 ml) in the left-hand elbow.

After mixing the ether of cellulose and benzyl alcohol dissolved in the benzene;

this was accompanied by a change in volume of 0.0123 ml per gram (Table 3).

The thermal effect of dissolution proved to be 2.55 cal per gram. For this system, therefore, $\frac{\Delta v/m}{Q} = \frac{0.0123}{2.55} = 48 \cdot 10^{-4}$. The values of the thermal effect of diluting solutions of the ether of cellulose and benzyl alcohol in benzene, listed in Table 4, were calculated on the basis of this ratio. These figures show that the integral volumetric effect of diluting the ether of cellulose and benzyl alcohol to a concentration of 0.04% equals $-(0.0123 + 0.0090) = -0.0213$ ml per gram, and that, hence, the effect of dilution from 2% to 0.04% is more than 40% of the total dissolution effect, whereas the effect of dilution from 5% to 0.5% is only some 6% of this figure.

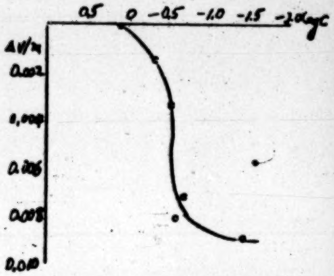

Fig. 4. Volumetric effects of diluting solutions of the ether of cellulose and benzyl alcohol in benzene.

When solutions of polystyrene in benzene are diluted step by step from 5% to 0.025%, no change in the volume is observed. It is possible that the bend in the $\frac{\Delta v}{m}$ – C curve lies in the region of concentrations below 0.025%; this is probable, because the bend in the curve of the scattering of light by the lyophobic ash obtained from these solutions of polystyrene lies in this region of solution concentration [6].

Nor did we find any volumetric effect when we diluted aqueous solutions of pectin from the initial concentrations of 2%-0.2% to concentrations of 0.2%-0.1%.

Nor was the dilution of nitrocellulose in dioxane accompanied by any change in the volume of the system: the values of $\frac{\Delta v}{m}$ we secured did not exceed the experimental error.

Evaluation of Results

Inasmuch as the swelling and the dissolution of nitrocellulose in acetone are accompanied by the evolution of heat, it must be assumed that in this system the energy of adhesion (solvation) is greater than the energy of cohesion. Swelling is unrestricted in such systems, and dissolution should be complete. But this does not exclude the association of the solute's molecules in consequence of the forming of, say, hydrogen or dipolar bonds. The life of such bonds is very brief, and the part played by such association is negligible in systems consisting of low-molecular substances; but such association does become important in solutions of high-polymers, even when the number of bonds is relatively low compared to the total number of atom groups capable of interassociation, since the probability of the formation of new bonds must rise greatly in adjacent molecules. One of the present authors has put forward the hypothesis [5] that in some region of fairly low concentrations a rather sharp transition must exist from the state of random and relatively uniform distribution of high-polymer molecules in solution to a discrete system of distribution of the associations of these molecules. This hypothesis has been confirmed by various indirect experimental data, especially, on the optical properties of the lyophobic ash obtained from high-polymer solutions, etc. [6].

The data cited in the present paper indicate that in the nitrocellulose – acetone system an appreciable energy effect of dilution is detected in some region of low concentrations. This effect may be attributed to the decomposition of the associations that occurs in this region, accompanied by the solvation of the atom groups liberated from their mutual bonds.

It is evident that the existence of a negative volumetric effect (and, hence, the evolution of heat) when solutions of nitrocellulose in acetone or of the ether of cellulose and benzyl alcohol in benzene are diluted signifies that $\Delta H_{12} > \Delta H_{22}$, i.e., that the solvation energy is greater than the energy of association, because the increase in volume (absorption of heat) occurring as the result of the rupture of the bonds between the nitrocellulose molecules when the associations break down (evidently, these are principally the bonds between the hydroxyl groups and the infrequent carboxyl groups) is more than balanced by the decrease in volume (evolution of heat) due to the solvation of these liberated groups by the acetone. The converse takes place when solutions of nitrocellulose are diluted in ethyl acetate, the molecules of which apparently possess less solvation energy than the acetone molecules with respect to nitrocellulose; here $\Delta H_{12} < \Delta H_{22}$, while the rupture of the associations during dilution involves a change in the entropy of the system.

A similar relationship exists in the systems consisting of the ether of cellulose and ethyl alcohol and benzene and of the ether of cellulose and ethyl alcohol and ethyl acetate. As for benzene, it is obvious that the energy of its bond to the molecules of the ether of cellulose and ethyl alcohol may be less than the energy of the hydrogen bonds between the nonetherized hydroxyl groups of the cellulose ether, wherein it differs from the binding energy of the benzene to the ether of cellulose and benzyl alcohol. But it would seem that the binding energy between ethyl acetate and the ether of cellulose and ethyl alcohol ought to be greater than the ether's binding energy to benzene, and the $\Delta H = \Delta H_{12} - \Delta H_{22}$ effect resulting when the associations of the ether of cellulose and ethyl alcohol are ruptured ought to have, if not a negative value (evolution of heat and diminution of volume), then in any event a smaller absolute positive value than for the dilution of benzene solutions. The opposite is true, however, and this may be explained as due to the fact that the equation given above does not describe the phenomenon completely. At bottom, $\Delta H = \Delta H_{12} - \Delta H_{22} - \Delta H_{11}$, with ΔH_{11} fairly large in the case of ethyl acetate, i.e., the observed positive volumetric effect, which is larger than for diluted benzene solutions, occurs not only because of the rupture of the associations of the ether of cellulose and ethyl alcohol, but also because of the weakening of the bonds between the ethyl acetate molecules that solvate the ether of cellulose and ethyl alcohol.

The conjectural explanation for the absence of any observed volumetric effect when polystyrene solutions are diluted is given above, in the experimental section. As for the null effect of diluting aqueous solutions of pectin or solutions of nitrocellulose in dioxane, the latter might possibly be explained as due to the approximate equality of $\Delta H_{22} = \Delta H_{12}$, i.e., the identity of the binding energies (of the carboxyl and hydroxyl groups) between the pectin molecules themselves and between these molecules and those of the water that solvates them, and of the nitrocellulose molecules with one another and with the dioxane.

SUMMARY

1. A dilatometric method has been employed to determine the energy effects of diluting high-polymer solutions.

2. A new type of dilatometer is described, which makes it possible to determine the volumetric effects of dilution with a precision of 0.001 ml, corresponding to

a thermal effect of the order of 0.1 cal.

3. A study has been made of the volumetric effects of diluting solutions of nitrocellulose in acetone and of the ether of cellulose and benzyl alcohol in benzene from various initial concentrations (starting with 15%) down to various final concentrations (as low as 0.025%). The volumetric effects of dissolving dry nitrocellulose in acetone and the ether of cellulose and benzyl alcohol in benzene have been determined.

It has been found that all the volumetric effects are negative within this range of dilutions. They are insignificant at high concentrations and rise sharply in the region of dilutions below 0.3%, where 25% of the total effect of dissolving the dry substance takes place for nitrocellulose, and as much as 40% for the ether of cellulose and benzyl alcohol. The volumetric effects of diluting nitrocellulose in ethyl acetate are positive, while the nature of the curve is similar.

4. Positive, negative, or null volumetric effects of dilution have been found for solutions of several other high-polymers (the ether of cellulose and ethyl alcohol, polystyrene, and pectin).

5. The results obtained have been explained on the basis of Glikman's previous hypothesis concerning the sharp change in the degree of association of the high-polymer molecules in some region of low concentrations.

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MOLECULAR COMPOUNDS OF ALUMINUM BROMIDE WITH AMMONIA AND AROMATIC HYDROCARBONS

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Gustavson [1] was the first to make a study of the molecular compounds of the aluminum halides with the aromatic hydrocarbons. These compounds are quite interesting, both from the standpoint of an explanation of the Friedel-Crafts reaction and as regards the chemistry of the coordination compounds of the aluminum halides.

Neminsky and Plotnikov [2] were the first to make a physicochemical investigation of the system aluminum bromide - benzene, finding that this system was a nonconductor.

A saturated solution of aluminum bromide in benzene exhibits hardly noticeable conductivity. Wohl and Wertyporoch [3] estimate the conductivity of a 20% solution of aluminum bromide in benzene to be $< 10^{-9}$ mho.

The thermal analysis of the aluminum bromide - benzene, aluminum bromide - toluene, and aluminum bromide - xylene systems, carried out by B.N.Menshutkin [4], showed that aluminum bromide does not form chemical compounds with the foregoing hydrocarbons. Cryoscopic investigations of a solution of aluminum bromide in benzene, made by various authors [5], have shown that aluminum bromide exists in the form of dimer molecules in a benzene solution, and that in the gaseous state its molecular weight corresponds to the formula Al_2Br_6 at temperatures below 440°.

The researches of Ulich and Nespital [6], as well as those of Plotnikov, Sheka, and Yankelevich [7], on the electrostatic properties of a solution of aluminum bromide in benzene have shown aluminum bromide is nonpolar both in concentrated and in dilute benzene solutions. Only in highly diluted solutions, at concentrations below 2% does molar polarization grow rapidly, the extrapolated value of the moment being about 5 D for infinite dilution.

Aluminum bromide dissolves in benzene and toluene with the absorption of heat. The heat of solution of aluminum bromide in benzene is -1.4 cal (per mol of $AlBr_3$) and in toluene is -0.7 cal, as Plotnikov and Yakubson [8] have shown. The molar refraction of aluminum bromide in benzene is 32.40 and 32.65 in the vapor state, according to Korshak, Lebedev, and Fedoseyev [9].

The results of physicochemical research indicate that aluminum bromide retains its individual properties in benzene and toluene solutions, not forming chemical compounds with these solvents. The departure from additivity of the properties of solutions of aluminum bromide in aromatic hydrocarbons that occurs at highly diluted solutions may possibly be the result of the solvation of the monomeric molecules of aluminum bromide that are produced as the result of dilution of the solutions, as has been pointed out by Plotnikov, Sheka, and Yankelevich [7], but it is not impossible that these discrepancies are the result of the action of moisture (owing to the high sensitivity of these systems to moisture), which may play a decisive part in the physicochemical measurements of highly diluted solutions. In any event, all the physicochemical researches of various authors give the same answer to the problem of the absence of chemical interaction between aluminum bromide and aromatic hydrocarbons in moderately diluted and concentrated solutions. In fact, the endeavors of many researchers to produce a coordinated compound of aluminum bromide and benzene or toluene by crystallizing these solutions met with failure.

These solutions crystallize with the aluminum bromide separating out. The results of these investigations are completely contradicted by the work of Plotnikov and Gratsiansky [10], who point out that a coordination compound of aluminum bromide and benzene, with the composition of $AlBr_3 \cdot C_6H_6$, crystallizes out of benzene solutions containing less than 70% of aluminum bromide.

Gustavson [11] made a study of the crystals formed during the crystallization of solutions of aluminum bromide in benzene and toluene, the concentration of which corresponds to the formulas $AlBr_3 \cdot 3C_6H_6$ and $AlBr_3 \cdot C_7H_8$, i.e., with 50 to 53% of aluminum bromide, and found that the crystals were aluminum bromide. Norris and Rubinstein [12] evaporated in vacuum a toluene solution of aluminum bromide with the same composition. Aluminum bromide separated out upon crystallization.

Menshutkin [4] investigated the crystalline phase produced in the crystallization of a benzene solution containing ~ 73% of aluminum bromide and found that the crystals were aluminum bromide; he added that the crystals were acicular in shape, and sometimes were lamellae. It may be that this unusual form of the crystals of aluminum bromide was what confused the authors who took them to be a quite unstable compound of aluminum bromide and benzene.

Molecular compounds of aluminum bromide and aromatic hydrocarbons are formed when a third component is present. Thus, Gustavson [11] was the first to produce a molecular compound of aluminum bromide with benzene or toluene by passing hydrogen bromide through a benzene or toluene solution of aluminum bromide. Gustavson assigned the following formulas:

$$AlBr_3 \cdot 3C_6H_6 \quad \text{and} \quad AlBr_3 \cdot 3C_7H_8,$$

to the resulting compounds.

Subsequent researches, however, especially the investigations of Korshak, Lebedev, and Fedoseyev [5], have shown that hydrogen bromide enters into the composition of Gustavson's coordination compounds, and that ternary coordination compounds with the composition:

$$Al_2BR_6 \cdot 6C_6H_6 \cdot HBr \quad \text{and} \quad Al_2Br_6 \cdot 6C_7H_8 \cdot HBr$$

are formed when hydrogen bromide is passed through a solution of aluminum bromide. Gustavson himself [13], in his later papers, pointed out that some coordination compounds of the aluminum halides with hydrocarbons are ternary molecular compounds that contain a hydrogen halide. Thus, he produced the following coordination compounds in a crystalline state:

$$Al_2Cl_6 \cdot 2[C_6H_3((CH_3)_2CH)_3] \cdot HCl,$$
$$Al_2Br_6 \cdot 2[C_6H_3((CH_3)_2CH)_3] \cdot HBr,$$
$$Al_2Cl_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HCl.$$

The last of these coordination compounds was likewise produced by Norris and Ingraham [14] by Gustavson's method, they confirmed its composition. They also secured compounds with symmetrical triethylbenzene and mesitylene: $Al_2Br_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HBr$ and $Al_2Br_6 \cdot 3C_6H_3(CH_3)_3 \cdot HBr$.

Norris and Wood [15] secured the crystalline coordination compound:

$$Al_2Br_6 \cdot C_6H_3(C_2H_5)_3 \cdot HBr,$$

and pointed out that the hydrogen bromide in these ternary coordination compounds may be replaced by ethyl bromide. They secured the following coordination compounds: $Al_2Br_6 \cdot C_6H_3(C_2H_5)_3\ C_2H_5Br$ and $Al_2Br_6 \cdot C_6H_3(CH_3)_3 \cdot C_2H_5Br$.

The formation of ternary coordination compounds as the result of the action of a third component upon the system aluminum bromide - aromatic hydrocarbon is likewise borne out by the work of Plotnikov and his associates. They secured the following coordination compounds, for example:

$KHal \cdot AlBr_3 \cdot nC_6H_6$ [16]; $TlBr \cdot AlBr_3 \cdot 2C_6H_6$ [17]; $CuBr \cdot AlBr_3 \cdot C_7H_8$ [18].

Evidently, the formation of ternary coordination compounds of aluminum bromide with aromatic hydrocarbons is due to the interaction of the polar molecules of the third component with the polarized molecules of the hydrocarbon and aluminum bromide. Aluminum bromide, benzene, and symmetrical triethylbenzene are nonpolar. The dipole moment of toluene is 0.4 $\underline{D}$ [19]. The third component, under whose influence the coordination compound is formed, has an appreciable dipole moment. The halides of the alkali metals possess dipole moments of the order of 5-7 $\underline{D}$ [19], while that of ethyl bromide is 2.0 $\underline{D}$ [19]. Least polar is hydrogen bromide, whose dipole moment in the gaseous state is 0.78 $\underline{D}$, but as Weith, Hobbs, and Gross [20] have shown, the electric moment of hydrogen bromide in a benzene solution is 1.08 $\underline{D}$, i.e., nearly one and a half times as much.

The present paper describes experiments aimed at the securing of ternary coordination compounds of aluminum bromide with ammonia and aromatic hydrocarbons (benzene and toluene). The electric moment of ammonia is 1.46 $\underline{D}$ [19], which is adequate for the production of rather stable coordination compounds with aluminum bromide and the hydrocarbons. Passing gaseous ammonia through benzene or toluene solutions of aluminum bromide, we succeeded in recovering coordination compounds of the following composition:

$$AlBr_3 \cdot 3NH_3 \cdot C_6H_6,$$

$$AlBr_3 \cdot 5NH_3 \cdot C_6H_6,$$

$$AlBr_3 \cdot 3\tfrac{1}{2}NH_3 \cdot C_7H_8.$$

Ephraim and Millman [21] found that aluminum bromide absorbs ammonia at room temperature, forming the hexammine $AlBr_3 \cdot 6NH_3$.

According to Klemm and Tanke [22], aluminum bromide forms ammoniates with 1, 3, 5, 6, 7, 8, and 14 molecules of ammonia per molecule of $AlBr_3$. The higher ammoniates are intrusion products with an ionic lattice. The ammonia molecules are located in between the aluminum and halogen ions. It is natural to assume that when a ternary coordination compound is formed, the polarized molecules of the aromatic hydrocarbon become part of the inner sphere of the coordination compound, partially replacing the ammonia. In its general form, the structure of the ternary coordination compound may be represented by the following formula:

$$[Al \cdot nNH_3 \cdot mC_6H_6]X_3.$$

The ternary coordination compound with toluene contains a fractional number of ammonia molecules. This confirms the general tendency of the aluminum halides to form coordination compounds containing twinned molecules of the aluminum halide - Al_2X_6, which was pointed out by Kalbukov and Sakhanov some time ago [23].

The problem of the structure of these complicated compounds: whether they are multinuclear coordination compounds, as has been conjectured by the present author [24] for the complicated compounds of aluminum iodide, or their molecules consist of a coordination cation and a coordination anion, as shown in the structural formulas advanced by Wohl and Wertyporoch [25], requires special investigation.

EXPERIMENTAL

1. Aluminum Bromide - Ammonia - Benzene

The aluminum bromide was prepared by reacting bromine with aluminum shavings. The resulting product was distilled into a drawn-out test tube, which was sealed after it had been filled with aluminum bromide.

The benzene and toluene were freed of their thiophene by repeatedly agitating them with concentrated sulfuric acid; then they were washed with a dilute solution of alkali, desiccated above calcium chloride and metallic sodium, and distilled over metallic sodium.

The ammonia was produced in a Bunsen flask by reacting a concentrated aqueous solution of ammonia with solid caustic potash. The gaseous ammonia was desiccated in two towers and a U-shaped tube, all filled with chemically pure solid caustic potash.

The fused aluminum bromide was poured into a small Bunsen flask fitted with a calcium chloride tube containing solid potassium hydroxide. After it had hardened, benzene was added to it. The gas outlet tube was plunged into the solution, and the ammonia then bubbled through the solution, part of it dissolving therein.

To prevent the gas outlet tube from clogging up, it terminated in a funnel-shaped widening. The solution of aluminum bromide in benzene was slightly yellowish in color, but the solution lost its color as the ammonia was passed through. The reaction was accompanied by the evolution of a large amount of heat. The solution grew very warm, and a film formed on the surface, which disappeared when the solution was stirred.

The ammonia was passed through the solution in small batches for about an hour, the solution remaining transparent nearly all that time. Only toward the end of the reaction did an abundant white, finely crystalline precipitate settle out. The mother liquor was decanted into a Bunsen flask under anhydrous hydrogen under pressure. The precipitate was washed with anhydrous benzene. The wash benzene was added to the mother liquor, which was placed in an exsiccator with phosphoric anhydride and paraffin to crystallize. A day or two later transparent crystals made their appearance on the walls; they crumbled into a white powder when desiccated in vacuum or in a current of anhydrous hydrogen. Two series of tests were run. One series was run with a solution containing 13 g of aluminum bromide to 106 g of benzene (~ 11%); the other series using a solution that contained 28.5 g $AlBr_3$ to 112.5 g of benzene (20.2%).

The crystals that were crystallized out of the mother liquor and were washed with benzene were desiccated by keeping them for a long time above phosphoric anhydride in a vacuum exsiccator. The finely crystalline white powder thus produced underwent no noticeable change when exposed to the air. It is decomposed by water with effervescence. The aqueous extract contains benzene in the form of fatty drops, as well as ammonia, which is readily driven off by heating the solution with alkali. Ammonia is driven off when the crystals are heated in a test tube. Drops of benzene settle on the upper wall of the test tube, with a white sublimate, evidently $AlBr_3$, appearing somewhat lower down the wall. An earthy mass remains at the bottom of the test tube. The coordination compound decomposes without melting when heated in a sealed capillary to 260°. A white film appears on the walls of the capillary, and the powder is converted into a gray earthy mass.

The percentage of bromine and ammonia in the substance we had produced was determined by analysis. A weighed batch was decomposed with water, and the bromine in the resultant solution was determined by the Volhard method.

A titrated solution of alkali was added to the solution to determine the ammonia. The solution was evaporated to 1/3 its volume, until all the ammonia was driven off. The excess alkali was titrated back with acid. Analysis showed that molecular compounds of aluminum bromide with ammonia and benzene of varying composition were formed, depending on the concentration of the benzene siutions used in the experiment. In the first series of tests, using more dilute solutins containing $\sim$11% $AlBr_3$, a molecular compound corresponding approximately to the formula $AlBr_3 \cdot 3NH_3\ C_6H_6$ is formed:

92.26 mg substance. 8.4 ml $AgNO_3$; N_{AgNO_3} 0.0848. 92.26 mg substance: 10.6 ml KOH; N_{KOH} 0.06812. Found %: Bromine 61.7; ammonia 13.3. Calculated from the formula $AlBr_3 \cdot 3NH_3 \cdot C_6H_6$, % Bromine 60.5; ammonia 12.9.

In the second series of tests, with more highly concentrated solutions of aluminum bromide in benzene, containing 20.2% by weight of aluminum bromide, the molecular compound secured by crystallizing the mother liquor and washing with benzene had the formula $AlBr_3 \cdot 5NH_3 \cdot C_6H_6$:

67.79 mg substance: 5.63 ml $AgNO_3$; N_{AgNO_3} 0.0848. 67.79 mg. substance: 11.15 ml KOH; N_{KOH} 0.0688. Found %: Bromine 56.3; ammonia 19.2. Computed from the formula $AlBr_3 \cdot 5NH_3 \cdot C_6H_6$, %: bromine 55.79; ammonia 19.8.

The precipitates secured as the result of the reaction of gaseous ammonia with benzene solutions of aluminum bromide, washed with anhydrous benzene and desiccated either in vacuum or in a current of anhydrous hydrogen, did not look any different from the above-described molecular compounds of aluminum bromide with benzene and ammonia. They, too, decomposed when heated, giving off ammonia and benzene. But the composition of the precipitates varied within rather wide limits, depending upon the concentration of the aluminum bromide in the solution and the method used to desiccate the precipitates.

In the precipitates secured from solutions containing 25-30% aluminum bromide, we found the following percentages (after washing them with anhydrous benzene and desiccating them in vacuum):

Bromine		Ammonia	
77.37		-	
77.48	77.38	-	8.56
75.63	(mean value)	8.82	(mean value)
79.07		8.31	

The precipitates secured from solutions containing 10-15% of aluminum bromide, which were desiccated in vacuum, exhibited the following percentages:

bromine: 72.03; 69.89;
ammonia: - ; 17.71.

And, lastly, the precipitate secured from a 20% solution of aluminum bromide, which was desiccated in a current of anhydrous hydrogen, contained 64.64% of bromine and 13.82% of ammonia.

It is probable that the reaction of gaseous ammonia with aluminum bromide dissolved in benzene results in the formation of molecular compounds of varying composition. Their composition depends upon the solution concentration, the time the ammonia reacts with the solution, and the treatment given the precipitate.

2. Aluminum Bromide - Ammonia - Toluene

These experiments were conducted with solutions containing 20% by weight of aluminum bromide in toluene. The solution was dirty yellow and contained a slight quantity of a heavy, dark-brown oil, drops of which settled to the bottom of the reaction vessel.

The reaction of the gaseous ammonia with the toluene solution of aluminum bromide was performed in a reaction vessel chilled with an ice-salt mixture. The solution was decolorized as the ammonia passed through, and the oil disappeared. The ammonia was passed through in small batches for an hour. The solution remained transparent throughout, only at the end of the reaction did an abundant finely crystalline white precipitate settle out. The liquid was decanted off, while the precipitate was washed with anhydrous toluene.

The mother liquor and the wash toluene were placed in an exsiccator with phosphoric anhydride to crystallize.

The precipitates were desiccated in a current of anhydrous hydrogen. The substances secured were analyzed to determine their percentages of bromine and ammonia. The precipitate produced in the reaction vessel has the same composition as the precipitate produced by crystallizing the mother liquor and the wash toluene, the formula being: $AlBr_3 \cdot 3\frac{1}{2}NH_3 \cdot C_7H_8$.

a) Analysis of the precipitate in the reaction vessel. 166.30 mg substance: 14.30 ml $AgNO_3$; N_{AgNO_3} 0.0840. 166.30 mg substance: 18.93 ml KOH; N_{KOH} 0.0716. Found %: bromine 57.69, ammonia 13.89.

b) Precipitate, recrystallized from toluene: 96.48 mg substance: 8.33 ml $AgNO_3$, N_{AgNO_3} 0.0840. 96.48 mg substance. 11.52 ml KOH; N_{KOH} 0.0716. Found %: bromine 57.93; ammonia 14.56. Computed from the formula $AlBr_3 \cdot 3\frac{1}{2}NH_3 \cdot C_7H_8$, %: bromine 57.31; ammonia 14.25.

The resultant molecular compound of aluminum bromide, ammonia, and toluene is a finely crystalline white powder, fatty to the touch, and having the same external appearance as the corresponding molecular compound with benzene. It decomposes when heated, giving off ammonia and toluene. It decomposes without fusing when heated to 210° in a sealed capillary.

In conclusion, I wish to express my gratitude to Prof. V.A.Izbekov for the interest he has displayed in this research.

SUMMARY

1. Aluminum bromide forms coordination compounds with benzene and toluene when a third constituent, the polar molecules of which enter into the composition of the resulting ternary coordination compound, acts upon the system.

2. The reaction of gaseous ammonia with aluminum bromide in benzene or toluene results in the formation of molecular compounds that contain aluminum bromide, ammonia, and the aromatic hydrocarbon.

3. Coordination compounds of the following composition; $AlBr_3 \cdot 3NH_3 \cdot C_6H_6$; $AlBr_3 \cdot 5NH_3 \cdot C_6H_6$; and $AlBr_3 \cdot 3\frac{1}{2}NH_3 \cdot C_7H_8$ have been secured and their properties described.

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THE KINETICS OF THE ISOMERIZATION OF n-BUTANE IN THE LIQUID PHASE OVER ALUMINUM CHLORIDE

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The equilibrium ratio of n-butane to isobutane has been often determined experimentally and has been calculated from thermodynamic and spectroscopic data. We may mention the work of Frost [1,2,3], and of Moldavsky and Nizovkina [4], in which a bibliography on the subject may be found. But we know of only one paper [5], devoted to the kinetics of the isomerization of the butanes, the authors having isomerized n-butane in the presence of aluminum bromide and commented that "the order of the reaction" with respect to n-butane remained unclear to them.

We ran tests at temperatures ranging from 55° to 100° and lasting 20 to 840 minutes to convert n-butane into isobutane above aluminum chloride, which yielded a kinetic characteristic for the process of isomerizing n-butane.

In our tests, the n-butane was subjected to isomerization in test tubes of special design, made of stainless steel (capacity 60 ml), which were agitated in a glycerin thermostat. The temperature in the thermostat was regulated automatically, being kept within ±0.05° of the specified temperature. The raw material was n-butane, prepared by dehydrating n-butyl alcohol, hydrogenating the resulting butylenes, and carefully rectifying the hydrogenation product. The percentage of isobutane in the products of the test, after the hydrogen chloride had been removed and the isobutane had been desiccated, was established by means of its nitrobenzene point, as well as by its rectification curve. Whenever the percentage of isobutane was low (up to 10%), its concentration was determined by the mean of 3 to 5 determinations of the nitrobenzene point. The aluminum chloride was prepared for the experiments from the freshly received industrial product by subliming it from a mixture with aluminum powder, placed in an elbow-shaped sealed glass tube. Before the start of the experiment 1 mol of hydrogen chloride was introduced into the test tube for every 7 mols of n-butane. In all our tests we used 4.0 g of aluminum chloride and 20 to 21 g of n-butane. The pressure within the test tubes was not measured, but it obviously rose somewhat as the isobutane accumulated, i.e., it did not remain constant throughout the experiment.

The test results are given in Table 1. The test runs marked with an asterisk were run in parallel, the mean results being listed in the column headed "Depth of isomerization - experimental." We took these results as our basic ones, as being the most reliable of the given test series. As the temperature was raised, we

TABLE 1

Depth and Velocity of Isomerization of n-Butane as Functions of the Temperature and the Time of Contact

Test No.	Time of contact τ	log τ	$\log \log \frac{D}{D-M}$	Depth of isomerization		Rate of isomerization, $\underline{v}$
				$M_э$	M_p	
Tests at 55°						
55	40	1.602	$\bar{2}.518$	1.9	1.7	0.179
53	60	1.778	$\bar{2}.602$	2.2	2.5	0.182
44*, 46*	120	2.079	$\bar{1}.013$	5.3	5.3	0.175
52	360	2.556	$\bar{1}.535$	13.7	14.0	0.113
47*, 49*, 50*	600	2.778	$\bar{1}.798$	19.9	19.2	0.064
Tests at 70°						
17	20	1.301	$\bar{2}.230$	1.2	1.7	0.297
18	60	1.778	$\bar{2}.909$	5.7	5.9	0.308
6*, 7*, 9*	120	2.079	$\bar{1}.272$	11.5	11.5	0.277
10*, 13*, 14*	360	2.556	$\bar{1}.809$	26.1	26.1	0.116
19	600	3.778	$\bar{0}.086$	31.0	31.1	0.035
Tests at 85°						
68	20	1.301	$\bar{2}.672$	4.4	4.9	0.650
66	30	1.477	$\bar{2}.908$	7.4	7.8	0.660
58*, 59*, 61*	60	1.778	$\bar{1}.303$	16.1	16.1	0.596
62*, 63*	180	2.255	$\bar{1}.894$	36.4	36.4	0.204
64	360	2.556	0.309	43.2	43.0	0.020
Tests at 100°						
39	20	1.301	$\bar{1}.000$	11.6	12.0	1.197
27*, 29*, 32*	40	1.602	$\bar{1}.401$	24.9	24.9	1.045
41	60	1.778	$\bar{1}.631$	35.4	35.3	0.793
33*, 34*, 35*	120	2.079	0.019	51.4	51.4	0.241
40	180	2.255	0.233	55.4	55.5	0.038

decreased the duration of the "basic tests," though keeping the ratio of durations at 1:3, except for the temperature of 55°, where it was 1:5.

The variation of the depth and rate of isomerization of n-butane with the time of contact is well described by Equations (I) and (II), which are the equations previously proposed by Kolmogorov [6], Burlakov [7], Yerofeyev [8], and Kazeyev [9] in a somewhat different form, as modified by us:

$$\ln \frac{D}{D-M} = a \cdot \tau^{b} \quad (I); \qquad \underline{v} = (100 - \mathcal{E}) \cdot a \cdot b \cdot \tau^{b-1}, \quad (II)$$

where, in our case, $\underline{M}$ is the quantity of n-butane reacted (depth of isomerization of the n-butane), expressed in per cent of the initial product; $\underline{D}$ is the maximum depth of isomerization of n-butane at the given temperature, i.e., the ultimate value of $\underline{M}$; τ is the duration of the test in minutes; $\underline{a}$ is an equation parameter indicating the velocity level of the process of isomerizing n-butane and having the dimensions of $[\tau]^{-b}$; b is an equation parameter – a dimensionless quantity, that indicates the type of process involved in the isomerization of the n-butane; ε is the quantity of n-butane that has entered into the reaction by the time " τ", expressed in per cent of the total conversion at the conclusion of the reaction; and w is the rate of isomerization of the n-butane, expressed in per cent per minute, i.e.:

$$w = \frac{dM}{d\tau} \cdot \frac{100}{D} = \frac{d\varepsilon}{d\tau} .$$

TABLE 2

Data Characterizing the Isomerization of n-Butane as a Function of the Temperature

°C	D	b	log b	a	log a	τ_{max}	ε_{max}	w_{max}	M_{max}
55	25.1	1.126	0.0515	0.00107	$\bar{3}.0282$	62.1	10.8	0.182	2.7
70	33.0	1.170	0.0682	0.00158	$\bar{3}.1987$	47.7	13.2	0.313	4.4
85	43.6	1.239	0.0934	0.00288	$\bar{3}.4594$	29.6	17.5	0.662	7.6
100	56.5	1.295	0.1123	0.00488	$\bar{3}.6884$	19.5	20.4	1.203	11.5

The values of D found by us and listed in Table 2 represent the mean of two tests, the duration of which differed by 120 minutes, while the difference between the two depths of isomerization did not exceed 0.5%. The anomorphoses of Equation (i) were plotted from these mean values of D and M of the "basic experiments." Figure 1 and the data in Table 1 give an idea of the disposition of the other experimental points along the anamorphoses. The values of the parameters a and b, as well as of their logarithms, are listed in Table 2. The depths and rates of isomerization of n-butane, M_p and w, computed from Equations (I) and (II), respectively, are listed in Table 1; comparing them with the experimental data indicates that the discrepancies lie within the margin of experimental error involved in determining the concentration of the isobutane.

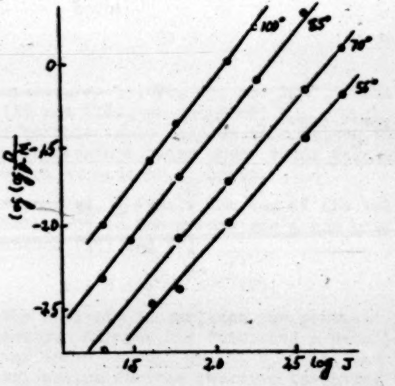

Fig. 1. Anamorphoses of the equations that indicate the relationship between the depth of isomerization of n-butane and the time of contact.

Inspection of the figures in Table 2 shows that the magnitude of the parameters a and b rises with a rise in temperature, the logarithms of these parameters rising linearly with 1/T (Fig. 2). Hence, the process of isomerizing n-butane in the presence of aluminum chloride is not of the discrete type.

The value of parameter b within the temperature range from 55 to 100°, 1.127-1.295, indicates that the reaction of isomerizing n-butane possesses an induction period within this temperature range. This peculiarity of the reaction is illustrated graphically by the curves in Fig. 3 which show the variation of the depth M and the rate w of the isomerization of n-butane with the contact time τ for the temperature of 70°. At the scale chosen, the point of inflection on the curve of M is barely noticeable, but the corresponding maximum in the w curve is quite prominent.

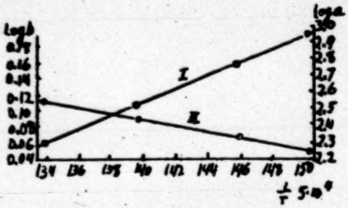

Fig. 2. Log a and Log b as functions of 1/T.
I - log a; II - log b

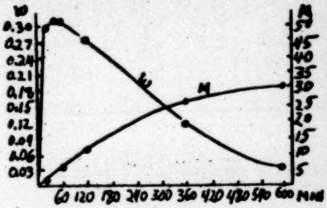

Fig. 3. Variation of the depth M and the rate w of isomerization of n-butane at 70° with the duration of the test. The hollow circles and the solid (black) ones are experimental points; the square with a dot in the center is a computed point.

The parameters a and b and the contact time τ_{max} that corresponds to the maximum rate are related together by Equation (III).

$$\tau_{max} = \left(\frac{b-1}{a \cdot b}\right)^{1/b}, \qquad (III)$$

which enables us to compute τ_{max} for the temperatures 55, 70, 85, and 100°. Substituting the respective values in Equations (I) and (II), we computed: M_{max}, ε_{max}, w_{max} (Table 2). Examination of the figures in this table lead us to conclude that the rate of isomerization of n-butane in the temperature range under study reaches a maximum at various values of ε, none of which exceeds 50, however.

According to Kazeyev, the energy of the process, E, equals the sum of the volume energy Q_a and the surface energy Q_b, whose relations to the parameters a and b of Equations (I) and (II) are expressed by Equations (IV) and (V):

$$a = A \cdot e^{Q_a/RT} \quad (IV), \qquad b = B \cdot e^{Q_b/RT} \quad (V),$$

where A is the catalysis coefficient; B is the activity factor; and the product $A \cdot B = L$ is the kinetic coefficient of activity. Kazeyev has furnished a detailed explanation of the physical meaning of the variables E, Q_a, Q_b, A, B, L, a, and b [8]. We have established the following relationships for the reaction involving the isomerization of n-butane:

$$a = 1328 \cdot e^{-9550/RT}, \quad b = 4.188 \cdot e^{-870/RT}, \quad L = 5570.$$

$$E = -9550 - 870 = -10420 \text{ cal/mol.}$$

The small size of Q_b compared to Q_a testifies to the negligible extent of the surface processes, i.e., that the reaction involving the liquid-phase isomerization of n-butane in the presence of aluminum chloride is largely homogeneous in nature. The small values of the parameter a indicate the low velocity level of the reaction. For the sake of comparison we cite figures on the change in the velocity level of liquid-phase isomerization of n-butane as a function of time (Table 1).

If we bear in mind the comparison made by Kazeyev between the activation energy and the "process energy," the coincidence of the value of the activation energy, 9.2 cal/mol, found for the isomerization of n-butane in the presence of aluminum bromide [5], with the value of the volume energy of the isomerization of n-butane in the presence of aluminum chloride, $Q_b = 9.55$ cal/mol, is worthy of note.

The following relationship holds good for the symbols we have adopted for the depth of isomerization of n-butane: ξ, according to Semenov [10], and M, according to Kazeyev [9]: $\xi = 100 \frac{M}{D}$. That is why the parameters a and b of Equation (I) and the parameters φ and θ' in the well-known Equation (VI) of Semenov [10]:

$$\xi = \frac{100}{1 + e^{-\varphi\theta}} = \frac{100}{1 + e^{-\theta'}}, \qquad \text{(VI)}$$

are related by the simple equation (VII):

$$\theta' = \theta \cdot \varphi = \ln (\xi/100) + a \cdot \tau^{b}. \qquad \text{(VII)}$$

Equation (VI) shows that at $\theta = 0$, $\xi = 50$; according to Semenov, the velocity passes through a maximum at this value of ξ. It follows from Equations (III) and (VII) that in that case $b = 1.694$, and hence the time $\tau_{50} = \left(\frac{0.694}{a \cdot b}\right)^{1/1694}$, i.e., $\tau_{max.} \neq \tau_{50}$ when n-butane is isomerized under the conditions chosen by us. Hence, the reaction involving the isomerization of n-butane, which we have classed as a chain reaction on the basis of the facts set forth above, does not obey Semenov's second fundamental law.

We concluded that when n-butane is isomerized in the temperature range 55-100°, there takes place a phenomenon called negative chain reaction by Academician Semenov [11].

SUMMARY

The reaction involved in the liquid-phase isomerization of n-butane above aluminum chloride is described by the generalized kinetics equations derived in the text. These equations establish a link between the depth and the rate of the reaction, on the one hand, and the contact time as a function of the effect of the medium in which the reaction takes place, and not in an isolated fashion as is done in the "classical kinetics" of J. van't Hoff, originating and developed within the framework of idealistic philosophic notions.

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THE PRINCIPAL PHYSICOCHEMICAL CONSTANTS OF THE n-ALKANES C_{13}-C_{19}[*]

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Knowing the accurate values of the principal physicochemical constants of the *n*-alkanes is required for their quantitative determination in petroleum products and for many other purposes. In particular, the quantitative determination of the *n*-alkanes by the thermal method[**] requires that we know the precise value of their temperatures of crystallization, recomputed for the 100% hydrocarbon. A slight error (say, 0.1-0.2°) in the value of the initial temperature of crystallization of the 100% hydrocarbon unavoidably results in an appreciable error in the quantitative determination of the n-alkane.

The crystallization temperatures and other constants of the C_5—C_{12} and C_{16} *n*-alkanes are known with adequate precision. The available data in the literature for the crystallization temperatures and other constants of the higher *n*-alkanes C_{13} - C_{15} and C_{17} -C_{19} are undependable, however. In order to get more accurate values of the principal physicochemical constants of the foregoing *n*-alkanes, the latter were prepared with a purity of 99.7-100.0% (molar), and their principal physicochemical constants were measured. Inasmuch as the results obtained are of general interest, we have decided to publish them in the form of a separate paper.

The crude C_{13} -C_{19} *n*-alkanes available to us[***], isolated from the cracking distillate of paraffin, were subjected to triple crystallization[****] (*n*-$C_{13}H_{28}$ from a 3:7 toluene - acetone mixture, and the other *n*-alkanes, C_{14} - C_{19}, from dichloroethane).

We always used four times as much solvent as the *n*-alkane. The principal constants of the initial *n*-alkanes are listed in Table 1, together with their initial crystallization temperatures and the yields of these same *n*-alkanes after their crystallization and the driving off of the solvent from a Wurtz flask.

The recrystallized C_{13} - C_{19} *n*-alkanes were distilled into a tower with the equivalent of 26 theoretical trays under the adopted operating conditions. The amount of each fraction taken was about 5% of the charged hydrocarbon. The initial temperature of crystallization was determined for all the fractions. Fractions with identical or adjacent crystallization temperatures were combined and were considered to be a refined n-alkane. The results of fractionating the C_{13} - C_{19} *n*-alkanes are shown in Figs. 1-7.

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[*] N.V.Milovidova secured n-tridecane in a pure state.

[**] The thermal method of determining n-alkanes quantitatively will be described in a separate paper.

[***] As has been stated above, the constants for n-hexadecane cited in the literature may be considered sufficiently reliable. Still, n-hexadecane was refined in the present research together with the other n-alkanes under the same conditions in order to check the efficiency of the refining method adopted by us.

[****] n-Tetradecane and n-nonadecane were crystallized twice.

TABLE 1

Results of Crystallizing the n-Alkanes

n-Alkane	Constants of the initial n-alkanes			Yield of the n-alkane after crystallization, % by weight	Crystallization temperature of the recrystallized n-alkanes
	Crystallization temperature	d_4^{20} (in vacuum)	n_D^{20}		
C_{13}	- 5.7°	0.7576	1.4251	65	- 5.4°
C_{14}	5.3	0.7645	1.4290	69	+ 5.7
C_{15}	9.2	0.7701	1.4320	75	9.6
C_{16}	17.2	0.7757	1.4352	72	17.7
C_{17}	20.5	0.7789	–	73	21.7
C_{18}	27.0	–	–	84	27.9
C_{19}	30.4	–	–	84	31.5

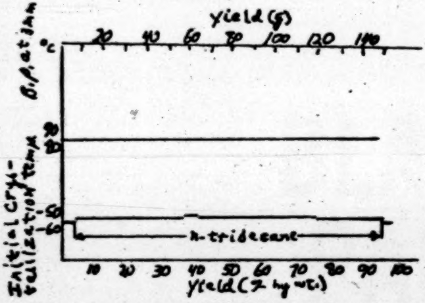

Fig. 1. Fractionation of n-tridecane.

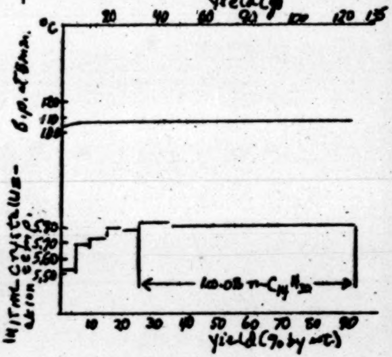

Fig. 2. Fractionation of n-tetradecane

The principal physicochemical constants were determined for the n-alkanes produced. The initial crystallization temperature ($t_{cryst.}$) and the lowering of the crystallization temperature at the point where 50% of the substance has crystallized ($\Delta t_{50\%}$) were determined in the apparatus and by the method described by Tilicheyev, Peshkov, and Yuganova [2]. The crystallization temperatures of 100% pure n-alkanes were computed from the formula: $t_{cryst.(100\%)} = t_{cryst.} + \Delta t_{50\%}$, where $t_{cryst.(100\%)}$ denotes the temperature of crystallization in the pure state (100% purity).

The density was determined in a 5-ml U-shaped pycnometer, described by Lipkin and his co-workers [7]. The absolute precision of measurement was 0.0002. The critical temperature of dissolution in aniline was determined by the method described by Tilicheyev and Dumskaya [1]. The measurements were made with a calibrated standard thermometer graduated to 0.1°. The initial crystallization temperature of the original aniline was 6.3°. n-Heptane (99.6% pure) exhibited a critical temperature of dissolution in this aniline of 69.4°. The index of refraction was measured with a

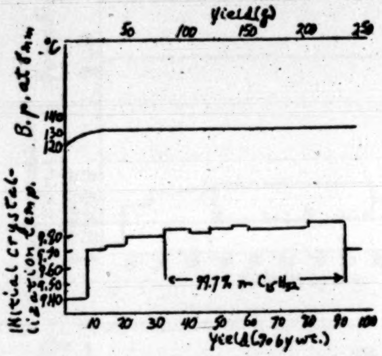

Fig. 3. Fractionation of n-pentadecane.

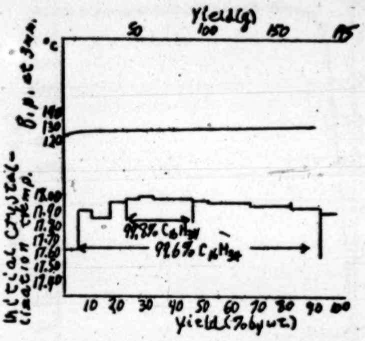

Fig. 4. Fractionation of n-hexadecane.

Pulfrich refractometer. The absolute precision of measurement was 0.00005. The density and the refractive index of the C_{17} – C_{19} n-alkanes were determined at temperatures above their crystallization temperatures and were reduced to 20° by means of the temperature coefficients listed in the paper by Deansley and Carleton [5].

The principal physicochemical constants of the purified n-akanes are listed in Table 2, while the curves of the crystallization temperatures of the n-alkanes C_{14}

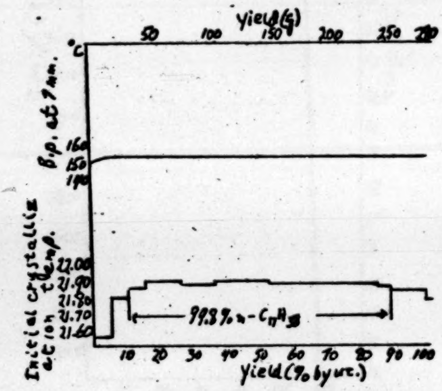

Fig. 5. Fractionation of n-heptadecane.

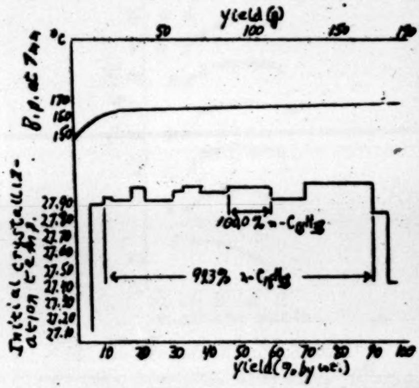

Fig. 6. Fractionation of n-octadecane.

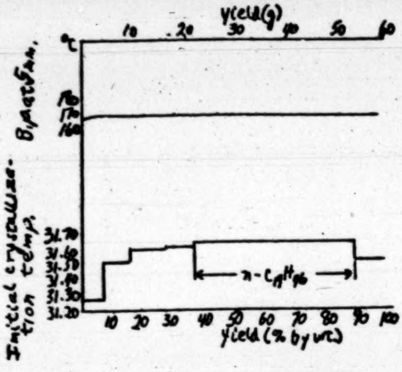

Fig. 7. Fractionation of n-nonadecane.

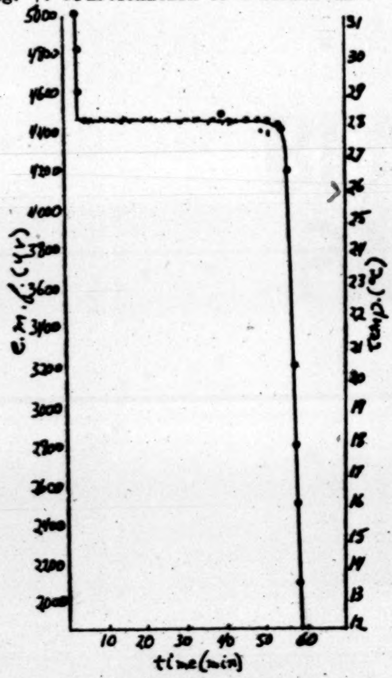

Fig. 9. Curve showing the crystallization temperature on n-octadecane.

Notation dots - upper thermocouple junction; crosses - lower thermocouple junction

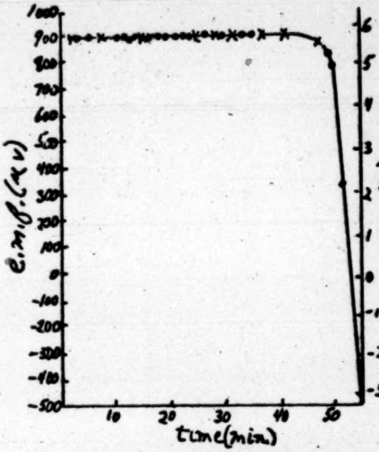

Fig. 8. Curve showing the crystallization temperature of n-tetradecane.

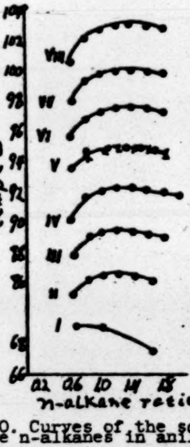

Fig. 10. Curves of the solubility of the n-alkanes in aniline.

I-n-C_7H_{16}; II-n-$C_{13}H_{28}$; III-n-$C_{14}H_{30}$; IV-n-$C_{15}H_{32}$; V n-$C_{16}H_{34}$ [notation in curve V: circles = dissolution temperature of n-$C_{16}H_{34}$ ($t_{cryst.}$ =18.06°) recovered from the cracking distillate of paraffin; crosses = dissolution temperature of n-$C_{16}H_{34}$ (t_{cryst} = 18 07°) recovered from standard cetane]; VI-n-$C_{17}H_{36}$ VII-n-$C_{18}H_{38}$ VIII-n-$C_{19}H_{40}$.

Table 2

The Physicochemical Constants of the Purified n-Alkanes C_{13} – C_{19}

n-Alkane	$t_{cryst.}$	$\Delta t_{50\%}$	t_{cryst} recomputed for the 100% hydrocarbon	d_4 (in vacuum)	d_4^{20} (in vacuum)	n_D^{20}	Critical temp of dissolution in aniline:	Volumetric hydrocarbon: aniline ratio	Aniline point	Purity molar %
C_{13}	-5.39±0.06°	0.06 ± 0.007°	-5.33±0.06°[10]	-	0.7561	1.4257	86.5°	1.0:1.2	86.5°	99.7
	(-5.5)[10]	-	-	-	(0.7559)[12]	(1.42541)[12]	-	-	-	-
C_{14}	+5.75±0.06	0.000(±0.007)	+5.75±0.06	-	0.7630	1.4291	89.4	1.0:1.0	89.4	100.0
	(+5.5)[9]	-	-	-	(0.7624)[12]	1.42688 [12]	(89.5)[8]	-	89.5[8]	-
C_{15}	9.81±0.06	0.060±0.007	9.87±0.06	-	0.7684	1.4322	92.2	1.0:1.2	92.1	99.7
	(9.6-9.8)[10]	-	-	-	(0.7687)[12]	(1.43199)[12]	-	-	-	-
C_{16}*	18.06±0.06	0.025±0.007	18.09±0.06	-	-	-	94.8	1.0:1.2	94.7	99.6
C_{16}**	18.07±0.06	0.025±0.007	18.10±0.06	-	0.7735	1.43451	94.9	1.0:1.4	94.8	99.6
	(18.145±0.003[5]	-	-	-	(0.77335)[5]	(1.43449)[5]	-	-	95[11]	-
	-	-	-	-	(0.7743)[12]	(1.43465)[12]	-	-	-	-
C_{17}	21.86±0.06	0.043±0.007	21.90±0.06	0.7769 at 22°	0.7783	-	97.4	1.0:1.2	97.3	99.8
	(21.92)[4]	-	-	(0.7767 at 22.5)[6]	-	-	-	-	-	-
C_{18}	28.10±0.06	0.000±0.007	28.10±0.06	0.7762 at 29°	0.7823	-	99.9	1.0:1.4	99.7	100,0
	(28.01)[4]	-	-	(0.7768 at 28°)[6]		-	-	-	-	-
C_{19}	31.75±0.08	0.066±0.008	31.82±0.08	0.7780 at 32°	0.7858	-	102.9	1.0:1.2	102.7	99.7

---

* Recovered from hydrogenated paraffin cracking distillate

** Recovered from standard cetane

and C_{18} are shown in Figs. 8 and 9. The curves of the solubility of the n-alkanes in aniline are shown in Fig. 10.

The curves of the crystallization temperature of purified n-tetradecane and n-octadecane (Figs. 8 and 9) exhibited no detectable slope, and the latter may therefore be considered to be 100% pure n-alkanes.

n-Heptadecane was refractionated under the conditions described above in order to purify it still further. The fractionation results are shown in Fig. 11. The values of the initial crystallization temperature (21.93 ± 0.06) and the $\Delta \underline{t}_{50\%}$ (0.025 ± 0.007) were determined for the n-heptadecane recovered after refractionation. The other constants were not determined, inasmuch as they would not have been changed appreciably. In terms of the 100% pure hydrocarbon, the temperature of crystallization of n-heptadecane is 21.96°.

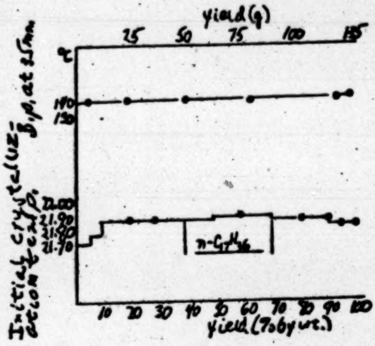

Fig. 11. Refractionation of n-heptadecane.

The final figures in the crystallization temperatures of the purified n-alkanes, in terms of the 100% pure hydrocarbons, are listed in Table 3.

TABLE 3

Crystallization Temperatures of Purified n-Alkanes, in Terms of 100% Hydrocarbons

n-Alkane	Purity of the actually recovered n-Alkane, molar %	$\underline{t}_{cryst.}$ in terms of the 100% hydrocarbon, experimental	$\underline{t}_{cryst.}$, according to the best data in the literature	Difference in the $t_{cryst.}$ between the experimental value and that given in the literature
n-$C_{13}H_{28}$...	99.7	-5.33±0.06°	-5.5°	+ 0.17°
n-$C_{14}H_{30}$...	100.0	+5.75±0.06	+5.5	+ 0.25
n-$C_{15}H_{32}$...	99.7	9.87±0.06	9.6 – 9.8	+ 0.17
n-$C_{16}H_{34}$...	99.6	18.10±0.06	18.145	– 0.04
n-$C_{17}H_{36}$...	99.8	21.96±0.06	21.92	+ 0.04
n-$C_{18}H_{38}$...	100.0	28.10±0.06	28.01	+ 0.09
n-$C_{19}H_{40}$...	99.7	31.82±0.08	–	–

The figures in Table 3 indicate that the values of the initial crystallization temperatures of the C_{13} – C_{15} and C_{17} – C_{18} n-alkanes found in the present research are higher than the best figures in the literature, exceeding them by 0.04-0.25°.

The high and accurately determined purity of the *n*-alkanes secured in the present research likewise acts as a guarantee that our values for the other constants are sufficiently dependable.

SUMMARY

1. The *n*-alkanes $C_{13} - C_{19}$ have been prepared with high purity (99.6-100%).

2. The principal physicochemical constants of the purified $C_{13} - C_{19}$ n-alkanes have been determined, *viz.*: the initial crystallization temperature, the density, the refractive index (n_D^{20}), and the critical temperature of dissolution in aniline.

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THE REACTION OF ALKYL-ARYL REAMINATION IN THE 2-DIALKYLAMINOPROPIONITRILES

A. F. Rekhli

With a view to producing the N-substituted amidines of 2-diethylaminopropionic acid, we made a study of the reaction of 2-diethylaminopropionitrile with aromatic amines. We know that under certain conditions the nitrile group can react with aromatic amines [1], yielding N-substituted amidines. The condensation of dicyandiamide [2] with amine hydrochlorides, resulting in the formation of substituted biguanides, points to the feasibility of such a reaction.

But when we condensed 2-diethylaminopropionitrile with the hydrochlorides of aromatic amines, we secured surprising results. Instead of the presumed reaction of the nitrile group with the aromatic amine, the 2-diethylaminopropionitrile breaks down into acrylonitrile and diethyl amine, the aromatic amine being added to the acrylonitrile that is formed. The process may be represented as follows:

$$(C_2H_5)_2N - CH_2 - CH_2 - CN + HCl \cdot H_2NR \longrightarrow HCl \cdot (C_2H_5)_2N - CH_2 - CH_2 - CN + H_2NR$$

$$HCl \cdot (C_2H_5)_2N - CH_2 - CH_2 - CN \longrightarrow (C_2H_5)_2NH \cdot HCl + CH_2{=}CH - CN$$

$$CH_2{=}CH - CN + H_2NR \longrightarrow R - NH - CH_2 - CH_2 - CN.$$

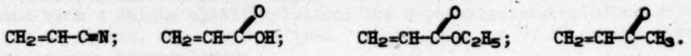
Thus, heating 2-diethylaminopropionitrile with hydrochlorides of the aromatic amines results in reamination, caused by the decomposition of the 2-diethylaminopropionitrile into diethyl amine and acrylonitrile. The process we have observed may be compared with similar decompositions in related systems. When 2-diethylaminopropionic acid is heated, for example, it breaks down into diethyl amine and acrylic acid [3]:

$$(C_2H_5)_2N - CH_2 - CH_2 - COOH \longrightarrow (C_2H_5)_2NH + CH_2{=}CH - COOH$$

When the ethyl ester [4] of 2-diethylaminopropionic acid is distilled, it likewise undergoes decomposition into diethyl amine and ethyl acrylate. The decomposition of 1-diethylaminobutanone-3 previously observed by us, in which diethyl amine is split off, is also a reaction of this type.

$$(C_2H_5)_2N - CH_2 - CH_2 - CO - CH_3 \longrightarrow (C_2H_5)_2NH + CH_2{=}CH - CO - CH_3.$$

All of the compounds considered hitherto have a tertiary nitrogen atom attached to the first carbon atom, with a double or triple bond at the third carbon atom, and as a result heating causes a dialkyl amine to split off, giving rise to an unsaturated compound with conjugated double bonds:

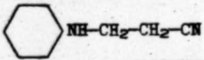


$$CH_2{=}CH{-}C{\equiv}N;\qquad CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}OH;\qquad CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5;\qquad CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3.$$

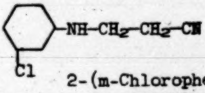
All that is required for a decomposition of this sort is the presence of a double or triple bond at the third carbon atom, the nature of the atom entering into this bond being of no importance $\left(>C{=}O,\ -C{\equiv}N \right)$.

The decomposition of all the compounds cited is of the same type. The nature of the atom added at the unsaturated bond affects only the way in which the reaction proceeds. 2-Diethylaminopropionic acid and its ester decompose when heated (160°); 2-Diethylaminopropionitrile undergoes absolutely no change when boiled (193°), as we have learned, it being decomposed only when its hydrochloride is heated (140-160°).

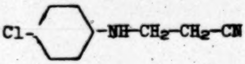
This reamination discovered by us may be employed as a new method for producing 2-arylaminopropionitriles. In this manner, i.e., by heating the hydrochlorides of aromatic amines with 2-diethylaminopropionitrile, we have secured the following 2-arylaminopropionitriles:



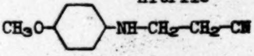
2-Phenylaminopropionitrile



2-(m-Chlorophenyl)-aminopropionitrile



2-(p-Chlorophenyl)-aminopropionitrile



2-(p-Methoxyphenyl)-aminopropionitrile

The properties and the melting points of the synthesized compounds agree fully with the figures for the corresponding 2-arylaminopropionitriles previously synthesized by us by directly adding aromatic amines to acrylonitrile [5]. In order to confirm the structure of the resulting compounds, 2-phenylaminopropionitrile was hydrolyzed to 2-phenylaminopropionic acid, which was identical with the acid first described by Bischoff and Nitz [6], who synthesized it in a different manner. Like the other nitriles, the 2-(p-methoxyphenyl)-aminopropionitrile synthesized by us is a white crystalline substance, m.p. 57-58° and b.p. 185-187° (3 mm). Elderfield and his co-workers [7] describe this product as an oil that distils without decomposition only in high vacuum.

In conclusion, it must be stated that one molecule of hydrochloric acid is required for the carrying out of the reamination described above, no matter whether it be used as the hydrochloride of a dialkylaminopropionitrile or as the hydrochloride of an aryl amine. If two molecules of hydrochloric acid are used, i.e., if a hydrochloride of an aryl amine is reacted with a hydrochloride of a dialkylaminopropionitrile, the reamination reaction will not take place.

EXPERIMENTAL

The 2-diethylaminopropionitrile was prepared by the Terentyev and Kost [8] method: heating acrylonitrile with diethyl amine over a water bath. The reaction product was distilled in vacuum. Yield 90%, b.p. 83-86° (17 mm).

2-Phenylaminopropionitrile. a) 6.3 g of 2-diethylaminopropionitrile (0.05 mol) and 60.0 g of aniline hydrochloride (0.46 mol) were heated for 2 hours in an open flask over a metal bath at 140-150°. After the resultant mass had cooled, it was treated with a dilute alkali solution: the 2-phenylaminopropionitrile, which separated out as an oil, soon crystallized. Yield, 5 g, or 67.8% of the theoretical, based on the aniline hydrochloride.

The product is soluble in alcohol, benzene, and dilute mineral acids, but is insoluble in water. 2-Phenylaminopropionitrile melted at 49° after distillation in vacuum (b.p. 146-148° at 3 mm) and crystallization from aqueous alcohol; a test sample mixed with the nitrile produced by us in a different manner exhibited no depression.

> 7.183 mg substance: 1.215 ml N_2 (20°, 731 mm). 5.584 mg substance: 0.970 ml N_2 (22°, 733 mm). Found %: N 18.95, 19.38. $C_9H_{10}N_2$. Computed %: N 19.17.

b) 8 g of the hydrochloride of 2-diethylaminopropionitrile (0.049 mol) and 4.7 g of aniline (0.05 mol) were melted for 2 hours in a flask fitted with an air-cooled condenser over a metal bath at 140-160°. After the reaction mass had cooled, it was diluted with water and treated with a solution of alkali, the oil that settled out crystallizing upon standing and after stirring with a rod. The substance was suction-filtered and washed with water; this yielded 4.1 g of 2-phenylaminopropionitrile, or 64% of the theoretical, based on the diethylaminopropionitrile; m.p. 49°; b.p. 145-146° (3 mm).

The hydrochloride of 2-phenylaminopropionitrile was prepared by adding alcoholic hydrochloric acid to an alcoholic solution of the base and precipitating it with ether; it is soluble in alcohol, but hydrolyzes partially when dissolved in water. White prisms from an alcohol-ether mixture, m.p. 128°. A test sample mixed with a hydrochloride of the nitrile prepared by us previously [5] exhibited no depression.

2-Phenylaminopropionic acid. 5 g of 2-phenylaminopropionitrile was boiled for 5 hours with 70 ml of concentrated hydrochloric acid in a flask fitted with a reflux condenser. The hydrochloric acid was driven off by heating in vacuum over a water bath. The residue was dissolved in a small quantity of water and neturalized with ammonia; the oil that settled out was extracted with ether. The ether was evaporated in a vacuum exsiccator; the residue, which was an oil, crystallized after standing for a few days in an exsiccator. Yield 3 g. The product fuses at 59° after recrystallization from a mixture of chloroform and petroleum ether (Bischoff and Nitz give the m.p. as 59-60°).

Reaction of the hydrochloride of 2-diethylaminopropionitrile with aniline hydrochloride. A mixture of 6.5 g of aniline hydrochloride (0.05 mol) and 8.1 g of 2-diethylaminopropionitrile hydrochloride was comminuted in a mortar and heated for 2 hours to 140-150°. During the heating, much hydrogen chloride was liberated, the mass thickened, and the color changed to a dark brown. After treating the mass with a solution of alkali, we secured a thick dark, oily product, which did not dissolve in benzene or water, was soluble in alcohol, and did not crystallize from aqueous alcohol or other solvents.

2-(m-Chlorophenyl)-aminopropionitrile. 8 g of m-chloroaniline hydrochloride (0.048 mol) and 6.3 g of 2-diethylaminopropionitrile (0.05 mol) were heated to 140-160° for 2 hours. The mass was treated with alkali, and the resulting oil was extracted with benzene; the benzene solution was desiccated with potash. After the potash had been removed and the benzene driven off, the residue was distilled in vacuum. 2-(m-Chlorophenyl)-aminopropionitrile distils at 184-185° (4-5 mm). Yield 3.7 g, or 42% of the theoretical. It crystallizes as white platelets from alcohol, m.p. 48°. A test sample exhibited no depression when mixed with 2-(m-chlorophenyl)-aminopropionitrile produced by us in another manner [5]. It is soluble in most organic solvents and dilute acids, but is insoluble in water.

> 4.680mg.substance: 0.647 ml N_2 (20°, 745 mm); 7.157 mg substance: 0.980 ml N_2 (24°, 755 mm). 0.1016 g substance: 0.0951 g $AgNO_3$.

0.1005 g substance: 0.0967 g $AgNO_3$: Found %: N 15.79, 15.63; Cl 19.53, 20.08. $C_9H_9N_2Cl$. Computed %: N 15.53; Cl 19.64.

The hydrochloride of 2-(m-chlorophenyl)-aminopropionitrile was produced by adding alcoholic hydrochloric acid to an alcoholic solution of the base and then precipitating it with ether. White prisms, m.p. 124-125°. It is soluble in water (partially hydrolyzing as it does so), and in dilute mineral acids, but is insoluble in ether.

0.1231 g substance: 5.74 ml 0.1N NaOH. Found %: Cl (ionic) 16.53. $C_9H_9N_2Cl \cdot HCl$. Computed %: Cl (ionic) 16.33.

2-(p-Chlorophenyl)-aminopropionitrile. 8 g of p-chloroaniline hydrochloride (0.048 mol) and 6.3 g of 2-diethylaminopropionitrile (0.05 mol) were heated for 2 hours to 140-160°. The method of treatment was similar to that set forth above. 2-(p-Chlorophenyl)-aminopropionitrile distilled at 186° (3-4 mm); yield 4 g, or 45% of the theoretical, based on the p-chloroaniline. It crystallizes as white platelets from aqueous alcohol, m.p. 72°. A test sample exhibited no depression when mixed with 2-(p-chlorophenyl)-aminopropionitrile that we had prepared by another method [5].

4.492 mg substance: 0.637 ml N_2 (20°, 736 mm). 4.941 mg substance: 0.706 ml N_2 (20°, 735 mm). 0.1006 g substance: 0.0981 g $AgNO_3$. Found %: N 16.00, 16.10; Cl 20.35. $C_9H_9N_2Cl$. Computed %: N 15.53; Cl 19.64.

The hydrochloride of 2-(p-chlorophenyl)-aminopropionitrile was prepared by adding alcoholic hydrochloric acid to an alcoholic solution of the base, and then precipitating it with ether. White prisms from an alcohol-ether mixture, m.p. 136°. A test sample exhibited no depression when mixed with the hydrochloride of 2-(p-chlorophenyl)-aminopropionitrile that we had prepared by another method.

2-(p-Methoxyphenyl)-aminopropionitrile. 8 g of p-anisidine hydrochloride (0.05 mol) and 6.3 g of 2-diethylaminopropionitrile (0.05 mol) were heated for 2 hours at 140-160°. The method of treatment was the same as that specified above.

2-(p-Methoxyphenyl)-aminopropionitrile distilled at 185-187° (3 mm). Yield 4.6 g, or 52% of the theoretical. It crystallizes in hexagonal platelets from aqueous alcohol, m.p. 57-58°. The nitrile is soluble in most organic solvents and in dilute mineral acids, but is insoluble in water.

5.045 mg substance: 0.725 ml N_2 (24°, 749 mm). 4.884 mg substance: 0.691 ml N_2 (24°, 750 mm). Found %: N 16.27, 16.04. $C_{10}H_{12}ON_2$. Computed %: N 15.90.

The hydrochloride of 2-(p-methoxyphenyl)-aminopropionitrile was produced by adding alcoholic hydrochloric acid to an alcoholic solution of the base and then precipitating it with ether. White prisms, m.p. 146°, soluble in water and alcohol, but insoluble in ether.

0.1305 g substance: 6.220 ml 0.1N NaOH. 0.1205 g substance: 5.598 ml 0.1N NaOH. Found %: Cl 16.90, 16.47. $C_{10}H_{12}ON_2 \cdot HCl$. Computed %: Cl 16.68.

Heating 2-diethylaminopropionitrile. 10 g of 2-diethylaminopropionitrile was heated for 3 hours in a two-necked flask fitted with a reflux condenser (temperature within the flask = 193°). Then the product was distilled at ordinary pressure, b.p. 192-193°; 8.7 g was distilled over, while the residue in the flask totaled 1 g. No diethyl amine was detected in a trap connected with the receiver and filled with dilute hydrochloric acid, after the acid had been evaporated. It may thus be considered as established that 2-diethylaminopropionitrile is not decomposed by heating.

Decomposition of the hydrochloride of 2-diethylaminopropionitrile. 8 g of the hydrochloride of 2-diethylaminopropionitrile was heated to 160-190° in a Claisen flask. After being diluted, the mass began to decompose, yielding acrylonitrile, which was driven off at 75-77°. A total of 2 g was driven off, or 77% of the theoretical. The residue consisted of diethyl amine hydrochloride, diethyl amine being produced when a concentrated solution of alkali was added to it. This yielded 1.3 g; the diethyl amine distilled at 56° after having been desiccated with caustic potash. It may be considered to be established that heating 2-diethylaminopropionitrile hydrochloride causes it to break down into diethyl amine and acrylonitrile.

SUMMARY

1. It has been established that the hydrochloride of 2-diethylaminopropionitrile, in contrast to the base, is decomposed by heat into diethyl amine hydrochloride and acrylonitrile.

2. A new method has been found for producing 2-aryl-aminopropionitriles: by heating 2-diethylaminopropionitrile with the hydrochlorides of the aromatic amines.

3. The mechanism of this reaction has been explored; it consists of the decomposition of 2-diethylaminopropionitrile into diethyl amine and acrylonitrile and the addition of ~~the~~ aromatic amine to the acrylonitrile in the presence of diethyl amine hydrochloride as a catalyst.

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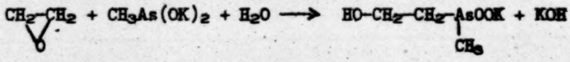
* See CB translation p. 1563 ff.

THE REACTION OF ETHYLENE OXIDE WITH SALTS OF ALKYL AND ARYL ARSENOUS ACIDS

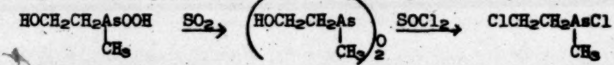
V. K. Kuskov and V. N. Vasilyev

In their reactions with the arsenites, sulfites, and nitrites of the alkali metals, ethylene oxide and the alkyl halides, as well as other alkylating agents, form salts of the alkyl arsenous acids, salts of the sulfo acids, and nitro compounds, respectively, i.e., products whose structure does not correspond to that of the original substances. When reacted with potassium arsenite, ethylene oxide forms potassium β-hydroxyethylarsenate [1], $HOCH_2CH_2AsO(OK)_2$.

When reacted with alkaline salts of alkyl arsenous acids, the alkyl halides give rise to dialkyl arsenic acids [2]. It may be supposed that here, too, ethylene oxide will react similarly, forming salts of β-hydroxyethylarsenic acids. We have carried out reactions of this type. When reacted with potassium methylarsenite, ethylene oxide forms potassium β-hydroxyethylmethylarsenate.



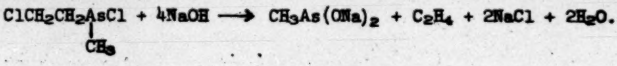
Acidulation and evaporation yielded the syrupy, unstable β-hydroxyethylmethylarsenic acid, which breaks down easily when heated. Reducing β-hydroxyethylmethylarsenic acid with sulfuric dioxide yielded β-hydroxyethylmethylarsine oxide. Subsequent treatment of the oxide with thionyl chloride by the method described for hydroxyethylarsenic compounds [3] yielded β-chloroethylmethylarsine:



$$HOCH_2CH_2\underset{CH_3}{AsOOH} \xrightarrow{SO_2} \left(HOCH_2CH_2\underset{CH_3}{As}\right)_2O \xrightarrow{SOCl_2} ClCH_2CH_2\underset{CH_3}{AsCl}$$

After distillation in vacuum we secured β-chloroethylmethylchloroarsine in the pure state, as a colorless, oily liquid.

β-Chloroethylmethylchloroarsine is decomposed by alkali solutions, especially when heated, evolving ethylene:



$$ClCH_2CH_2\underset{CH_3}{AsCl} + 4NaOH \longrightarrow CH_3As(ONa)_2 + C_2H_4 + 2NaCl + 2H_2O.$$

Methylarsine oxide was produced by acidulating the alkaline solution after decomposition.

Analogously to the above, we reacted ethylene oxide with potassium ethylarsenite and repeated the foregoing series of conversions, thus securing pure β-chloroethylethylchloroarsine as an oily liquid, which is likewise decomposed by alkalies.

Potassium phenylarsenite reacts with ethylene oxide like potassium methyl- and ethylarsenites.* The resulting products, however, including β-chloroethylphenylchloroarsine, decompose when distilled, even at 1 mm residual pressure.

We were unable to secure β-hydroxyethyldiphenylarsine oxide by treating an alkaline solution of diphenylarsine oxide with ethylene oxide; when the solution was acidulated, we recovered the original diphenylarsine oxide.

EXPERIMENTAL

β-Chloroethylmethylchloroarsine. A solution of 28.1 g of potassium hydroxide (0.5 mol) in 100 ml of water was mixed with 26.5 g of methylarsine oxide (0.25 mol) in a flask fitted with a stirrer and heated over a bath until the oxide had dissolved. Then the solution was cooled to room temperature, and ethylene oxide was passed through it for 10-15 minutes, with stirring, until the gain in weight was 12 g (0.27 mol); this caused the solution to warm up noticeably, and it was cooled with water. Then the solution was set aside to stand for 12 hours, after which it was diluted with 200 ml of water and acidulated against Congo with 10% sulfuric acid. The potassium sulfate that precipitated was filtered out, and the filtrate was evaporated at a temperature below 50° until it reached a syrupy consistency. 100 ml of benzene was twice added to the residue and then driven off in order to remove the last traces of water. β-Hydroxyethylmethylarsenic acid was extracted from the residue with 150 ml of absolute alcohol. Driving off the alcohol and desiccation in vacuum yielded 25 g of a barely yellowish oily liquid, β-hydroxyethylmethylarsenic acid. It was dissolved in 100 ml of water, a minute crystal of potassium iodide was added, and it was saturated for 2 hours with sulfur dioxide, at a temperature of 50° toward the close. The solution was set aside to stand for 12 hours, after which it was evaporated in vacuum and desiccated by mixing it with 100 ml of benzene and driving off the latter. The residue, 23 g of a thick yellowish oil, β-hydroxyethylmethylarsine oxide, was treated with 40 g of thionyl chloride in a flask fitted with a reflux condenser. The thionyl chloride was added drop by drop, and the reaction mass was chilled, to slow down the reaction. Toward the end the mass was heated to 50° over a water bath until no more gas was evolved.

The residue was distilled in vacuum; this yielded 22.1 g of β-chloroethylmethylchloroarsine, i.e., 52% of the theoretical, based on the methylarsine oxide, with a b.p. of 60-61° at 1 mm. A mobile, colorless liquid with a characteristic odor, soluble in benzene, dichloroethane, and alcohol. Water hydrolyzes it to the oxide. It is decomposed by aqueous alkali, evolving ethylene; the latter was determined by absorption in bromine water. When the residual solution is acidulated, methylarsine oxide is evolved. Analysis of the β-chloroethylmethylchloroarsine for arsenic was effected iodometrically; a weighed batch of the product to be analyzed was first treated with alkali until no more gas (ethylene) was evolved.

0.1652 g substance: 17.45 ml 0.1$\underline{N}$ I_2. 0.3178 g substance: 33.6 ml 0.1$\underline{N}$ $AgNO_3$. 0.3242 g substance: 20.00 g toluene: $\Delta \underline{t}$ 4.67°. Found %: As 39.67; Cl 37.5; $\underline{M}$ 175.5. $C_3H_7Cl_2As$. Computed %: As 39.5; Cl 37.5; M 188.9.

β-Chloroethylethylchloroarsine. 30 g (1 mol) of ethylarsine oxide was treated as described above. This yielded 11.7 g of β-chloroethylethylchloroarsine, or 23% of the theoretical, based on the ethylarsine oxide. β-Chloroethylethylchloroarsine is soluble in benzene, dichloroethane, and alcohol; it is decomposed by alkali, evolving ethylene.

SUMMARY

1. It has been shown that ethylene oxide is added to the arsenic in potassium salts of alkyl arsenous acids.

2. β-Chloroethylmethylchloroarsine and β-chloroethylethylchloroarsine have been synthesized and investigated.

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THE PROBLEM OF DETACHING RADICALS FROM ORGANOMETALLIC COMPOUNDS

VIII. THE SPLITTING OFF OF RADICALS BY THE ACTION OF ALUMINUM CHLORIDE AND FERRIC CHLORIDE UPON TRIPHENYLBISMUTH AND TRIPHENYLANTIMONY*

Z. M. Manulkin and A. N. Tatarenko

In our previous research, one of the present authors explored the strength of the Me—C bond, where Me = Si, Sn, or Pb, by the method of dealkylation; the dealkylating agents employed being iodine [1], hydrogen chloride [2], and the chlorides of mercury, aluminum, iron, and bismuth [3].

It is the objective of the present and subsequent papers to explore the strength of the Me—C bond in organometallic compounds of metals of Group V (Bi, Sb, As), employing aluminum chloride, ferric chloride, bismuth chloride, and the chlorides of some other metals as the dealkylating agents. At the same time we propose to study the part played by the cation of these cleaving chlorides in the dealkylation reaction and to shed light on the mechanism of the latter; lastly, we intend to determine the role of the solvent and the effect of the quantities of reagents used, as well as other factors, upon the course of the dealkylation reaction. Further research in this field enables us to set up a series of the metals according to the relative strength of their bonds with certain organic radicals, and to construct a series of the metal chlorides according to their activity in dealkylating a given organometallic compound.

As far as we know, there is practically no information in the literature upon the use of aluminum chloride or ferric chloride as dealkylating reagents for organometallic compounds of metals of Group V. We have made a study of the reaction of triphenylbismuth and triphenylantimony with ferric and aluminum chlorides.

The triphenylbismuth was synthesized by a Grignard reaction involving benzenemagnesium bromide and bismuth trichloride [4]; we managed to raise the output of triphenylbismuth considerably (to 82%) by carefully preparing anhydrous bismuth trichloride and varying the reaction conditions. We obtained a high yield of triphenylbismuth by the method described by Kocheshkov and Skoldinov [5]. The triphenylantimony was prepared by a Grignard reaction involving benzenemagnesium bromide and antimony trichloride [6]

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* Preliminary data reported to the meeting of the Tashkent branch of the D.I. Mendeleev All-Union Chemical Society, June 8, 1948.

A. The Action of Aluminum Chloride upon Triphenylbismuth and Triphenylantimony

1. The reaction of triphenylbismuth with 1 and 3 mols of aluminum chloride evidently proceeded as follows:

$$(C_6H_5)_3BI + AlCl_3 \longrightarrow BiCl_3 + [C_6H_5AlCl_2]. \qquad (1)$$

None of the permissible organoaluminum compound was recovered. Its formation was confirmed by the presence of benzene in the distillate (after decomposition with water), followed by its conversion into nitrobenzene and dinitrobenzene. The bismuth trichloride was confirmed by its melting point and by analysis. Thus, all three radicals are dearylated (not less than 80%) in both instances (1 and 3 mols).

2. The reaction of triphenylantimony with 1, 3, and 4 mols of aluminum chloride likewise results, in the main, in the complete detachment of all the three radicals, but with a lower yield than in the case of triphenylbismuth (56-74%). The end product of the reaction is antimony trichloride, recovered as antimony oxychloride and demonstrated by analysis. The reaction proceeds as follows:

$$(C_6H_5)_3Sb + AlCl_3 \longrightarrow SbCl_3. \qquad (2)$$

But when triphenylantimony is reacted with 1 mol of aluminum chloride, a quite minute quantity of products of the incomplete detachment of the radicals (diphenylantimony chloride and phenylantimony dichloride) is detected:

$$(C_6H_5)_3Sb + AlCl_3 \rightarrow SbCl_3 + (C_6H_5)_2SbCl + C_6H_5SbCl_2. \qquad (3)$$

This confirms that the Sb-C bond is stronger than the Bi-C one.

The reaction products are partially carbonized in all the three tests involving triphenylantimony. The next two experiments, made in a current of nitrogen with the aluminum chloride introduced gradually, indicate that carbonization occurs during heating, but that it does not take place during the same interval of time at room temperature. In the last test, traces of triphenylantimony dichloride were found; in all instances, however, the principal reaction product was antimony trichloride.

The question of the mechanism of the reaction of triphenylantimony with aluminum chloride requires further research. What we must find out is whether organoaluminum compounds are formed, as in the case of bismuth (1). No benzene is detected when the reaction products are distilled with steam.

As for chloroform, which we used as a solvent, it evidently does not enter into a Friedel-Crafts reaction in this instance, inasmuch as no diphenylchloromethane or triphenylmethane was detected. Preliminary experiments involving chloroform and triphenylbismuth (as well as triphenylantimony) have shown that no reaction takes place under the conditions of our reactions.

B. The Action of Ferric Chloride upon Triphenylbismuth and Triphenylantimony

1. The reaction of triphenylbismuth with 1 and 3 mols of ferric chloride results in the formation of bismuth trichloride (40% in the latter case). The reaction is as follows:

$$(C_6H_5)_3Bi + FeCl_3 \rightarrow BiCl_3. \qquad (4)$$

Thus, here, too, we find that all three radicals are dealkylated, but with a much lower yield. The presence of some benzene, as proved by decomposition with water and then by nitrating the traces of nitrobenzene, justifies the assumption that an unstable organoiron compound is formed. This problem requires further research, however.

2. The reaction of triphenylantimony with 3 mols of ferric chloride results in the formation of triphenylantimony dichloride (95%) and ferrous chloride. No benzene is found in the distillate after distillation with steam. The reaction may be represented as follows:

$$(C_6H_5)_3Sb + 2FeCl_3 \longrightarrow (C_6H_5)_3SbCl_2 + 2FeCl_2 \qquad (5)$$

Thus, ferric chloride does not act as a dealkylating reagent in this case. An oxidative-reducing process takes place, which corresponds with the data cited by Kocheshkov and Skoldinov [7].

EXPERIMENTAL

Synthesis of triphenylbismuth. The Grignard reagent was prepared from 3 g (0.12 gram-atom) of magnesium, 19 g (0.12 mol) of bromobenzene, and 150 ml of absolute ether. After the reaction mass had cooled, an ether suspension of 20 g (0.06 mol) of freshly prepared (from metallic bismuth and hydrochloric acid) and sublimed bismuth trichloride was added in small batches with constant stirring. Then the mixture was heated over a water bath for 3 hours. The ether was driven off, and the residue was reheated over an oil bath for 3 hours to 150° (bath temperature). After the reaction mass had cooled, the driven-off ether was added to it, and then it was decomposed, first with ice water, and then with ammonium chloride. The ether layer was separated and desiccated above calcium chloride. The residue left after the ether had been driven off was a yellow oil, which was set aside until it crystallized completely. The reaction product was purified by treating it repeatedly with absolute alcohol in the cold. The melting point of the purified substance was 75-76° (according to the literature [4], the m.p. is 77-78°). The yield was 23 g, or 82% of the theoretical. The compound was analyzed by Koton's method to determine its bismuth content.

Found %: Bi 47.73: $C_{18}H_{15}Bi$. Computed %: Bi 47.50.

Action of aluminum chloride on triphenylbismuth.* 2 g (0.01 mol) of freshly prepared (from aluminum and hydrogen chloride) and sublimed aluminum chloride was added in small batches during the course of 30 minutes to a solution of 4.4 g (0.01 mol) of triphenylbismuth in chloroform. The at first somewhat cloudy solution of triphenylbismuth becomes transparent, while a white precipitate settles out. As more aluminum chloride is added, the color of the solution changes from yellow to dark brown. The addition of aluminum chloride causes appreciable heating of the reaction mass. Then the mixture was heated for 6 hours over a water bath in a continuous current of nitrogen. The reaction product - a dark purple liquid and a yellow precipitate - was separated into two batches, which were analyzed separately.

Batch 1. To prove that organoaluminum compounds and bismuth trichloride were formed, the flask contents were decomposed with water, and the benzene was steam distilled and its presence demonstrated by nitration. What was left in the flask was a grayish powder of inorganic nature, consisting of bismuth oxychloride (proved qualitatively) and, obviously, the basic aluminum salt.

Batch 2. The transparent, dark-purple chloroform solution was separated from the precipitate by decantation for the same purpose. The chloroform was driven off, the residue dissolving nearly completely in ether. After the ether had been evaporated, there remained in the watch glass a bulky, milky-white precipitate, which decomposed rapidly when exposed to the air, burning with a typical, strongly smoky flame. No products of incomplete cleavage were found in the chloroform solution. The original precipitate (separated from the chloroform solution by decantation) yielded bismuth trichloride, with a melting point of 230° after recrystallization from absolute alcohol; the literature gives the m.p. as 225-230° [9]. The experiment was repeated under the same conditions in order to ascertain the yield of bismuth trichloride. The yield of bismuth trichloride was 80% of the theoretical.

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* The student A. B. Kagan participated in the synthesis of triphenylbismuth, as well as in the preliminary experiments on the reaction of the latter with aluminum chloride and ferric chloride.

Action of an excess of aluminum chloride upon triphenylbismuth. 5 g (0.03 mol) of aluminum chloride was added during the course of an hour to a solution of 4.4 g (0.01 mol) of triphenylbismuth in chloroform. Then the reaction mass was heated for 6 hours over a water bath, after which it was carefully decomposed with water, slightly acidulated with hydrochloric acid, and distilled with steam. The benzene floating on top of the distillate was extracted with ether and desiccated above calcium chloride. The ether was removed, and the presence of benzene was proved by its conversion into nitrobenzene. Neither diphenylchloromethane nor triphenylmethane was detected in the reaction products. The reaction flask contained a grayish precipitate, consisting of bismuth oxychloride and a small amount of carbonized matter. No compounds of an organic nature were found. The bismuth oxychloride was separated and analyzed.

Found %: Bi 79.96. BiOCl. Computed %: Bi 80.24.

Action of aluminum chloride upon triphenylantimony. Experiment 1. 3.5 g (0.01 mol) of triphenylantimony dissolved in 30 ml of chloroform was placed in a round-bottomed flask fitted with a reflux condenser, and 1.5 g (0.01 mol) of finely pulverized freshly prepared aluminum chloride was gradually added. This caused noticeable heating of the reaction mass, which was then heated for 5-6 hours over a water bath. The reaction product was carefully decomposed with slightly acidulated water and then distilled with steam. No benzene was found in the distillate. What was left in the reaction flask was a mass consisting chiefly of antimony oxychloride with a trace of a carbonized substance that dissolved neither in organic solvents nor in inorganic acids. A test for organic substances showed the presence of a minute quantity of the products of incomplete cleavage.

In order to recover the latter, the contents of the flask were treated with ether, all the organic compounds entering solution, while the antimony oxychloride and the carbon remained in the precipitate. Driving off the ether yielded a minute quantity of a substance, which was treated with petroleum ether; the solution possibly contained phenylantimony dichloride, while the residue yielded a product with a m.p. of 67° (diphenylantimony chloride); according to the literature [10], diphenylantimony chloride has a m.p. of 68°. The petroleum ether was driven off from the solution, and the residual product was treated in the cold with alcohol containing a slight quantity of hydrochloric acid; this caused the phenylantimony dichloride to enter solution, no triphenylantimony being detected in the residue. Evaporation of the alcohol yielded a substance with a m.p. of 57°, which agrees with the literature figure for phenylantimony dichloride (m.p. 58°) [11].

The antimony oxychloride was subjected to analysis as follows: a weighed portion of the substance was dissolved in concentrated hydrochloric acid, the antimony oxychloride entering into solution, while the carbonized matter was separated by filtration and then deducted from the initial weight. The solution was diluted until its reaction was weakly acid, and then it was saturated with hydrogen sulfide. The rest of the analysis followed the customary pattern.

Found %: Sb 70.04. SbOCl. Computed %: Sb 70.29.

Experiment 2. 2.7 g (0.007 mol) of triphenylantimony, 30 ml of chloroform, and 3 g (0.022 mol) of aluminum chloride were used. The experimental conditions differed from those of the preceding experiment solely in the quantity of aluminum chloride used (3 mols). Here, too, partial carbonization took place. No products of incomplete cleavage or other organic compounds were found. The principal reaction product was antimony trichloride, which was recovered as antimony oxychloride.

Found %: Sb 70.11. SbOCl. Computed %: Sb 70.29.

Experiment 3, using an excess of aluminum chloride (4 mols) under similar conditions yielded the same results.

Experiment 4. We used 4.2 g (0.012 mol) of triphenylantimony, 50 ml of chloroform, and 5.4 g (0.040 mol) of aluminum chloride. The experimental conditions differed from those of Experiment 2 only in that this experiment was carried out in a continuous current of nitrogen, while the aluminum chloride was added gradually. The results were the same. 1.56 g (74% of the theoretical) of antimony oxychloride was obtained.

Experiment 5. 5.7 g (0.042 mol) of aluminum chloride was added during the course of 3 hours in a continuous current of nitrogen to a solution of 5 g (0.014 g mol) of triphenylantimony in 50 ml of chloroform. The reaction mixture was not heated after the aluminum chloride was introduced, but was set aside to stand for 5 hours at room temperature in the stream of nitrogen. The reaction products did not carbonize. Decomposition and steam distillation left 6 g of a solid mass in the reaction flask. Extraction with ether indicated it contained traces of an organic substance with a m.p. of 141°, which corresponds to the m.p. of triphenylantimony dichloride; according to Kocheshkov and Skoldinov, the m.p. of triphenylantimony dichloride is 143° [12]. No other organic substances were found. The solid mass yielded 1.29 g of antimony oxychloride (56.2% of the theoretical, based on the triphenylantimony), which was subjected to analysis.

Found %: Sb 70.48: SbOCl. Computed %: Sb 70.29.

Action of ferric chloride upon triphenylbismuth. 2.5 g (0.01 mol) of freshly prepared (from iron and chlorine) ferric chloride was added in the course of 15 minutes to 4.4 g (0.01 mol) of triphenylbismuth dissolved in chloroform. The reaction gave no visible indications of taking place in the cold. The liquid turned dark brown when boiled over a water bath for 5-6 hours in a current of nitrogen. The reaction product was a brown solution with a red-brown precipitate. The precipitate consisted of inorganic compounds of iron (qualitative reaction with ammonium thiocyanate), plus a considerable quantity of bismuth trichloride. The precipitate was dissolved in hot absolute alcohol; evaporation of the latter and chilling caused bismuth trichloride to settle out, its presence being proved by its melting point (229°) and the formation of the sulfide.

The solution was likewise shown, by means of qualitative reactions, to contain ferric chloride and bismuth trichloride. Decomposition of the solution with water, followed by steam distillation demonstrated traces of benzene, which was proved by nitration.

Action of an excess of ferric chloride upon triphenylbismuth. 8.5 g of crystalline ferric chloride (0.03 mol in terms of the anhydrous product) was added to 4.4 g (0.01 mol) of triphenylbismuth dissolved in 50 ml of chloroform. The results of the experiment were the same. The presence of ferric chloride (with traces of the ferrous chloride) and of bismuth trichloride was proved qualitatively. The latter was recovered as the sulfide, totaling 2 g, or 40% of the theoretical, based on the triphenylbismuth).

Action of ferric chloride upon triphenylantimony. 5 g (0.03 mol) of ferric chloride was added gradually, with shaking, to 3.5 g (0.01 mol) of triphenylantimony dissolved in 30 ml of chloroform. The reaction apparently did not proceed in the cold. The mixture was heated for 5-6 hours over a water bath, after which it was steam distilled, no benzene being found in the distillate. The presence of ferric and ferrous chloride was qualitatively proved in the reaction products. Triphenylantimony dichloride, with a m.p. of 141° [12] was extracted from the solid mass remaining in the reaction flask by a benzene-ether mixture. The product was treated with an alcoholic solution of alkali to prove its nature. We recovered a compound with a m.p. of 210°, which corresponds to that of triphenylantimony dihydroxide; according to Kocheshkov and Skoldinov [7], the melting point of triphenylantimony dihydroxide is 210-215°. The yield of triphenylantimony dichloride was 4 g (95% of the theoretical). The latter substance did not dissolve in water, but was soluble in ether and benzine, readily soluble in benzene and hydrogen sulfide, and readily soluble, with slight heating, in oils (fish oil, peach oil, and castor oil).

SUMMARY

1. When reacted with triphenylbismuth and triphenylantimony (1, 2) in chloroform, aluminum chloride proves to be an active dearylating reagent; the reaction principally involves the splitting off of the three radicals.

2. When aluminum chloride is reacted with triphenylbismuth, organoaluminum compounds are evidently formed.

3. The dearylating reaction is harder to carry out with triphenylantimony, which confirms that the Sb–C bond is stronger than the Bi–C bond.

4. When ferric chloride is reacted with triphenylbismuth in chloroform, it likewise acts as a dearylating reagent, but a less active one than aluminum chloride.

5. When ferric chloride is reacted with triphenylantimony in chloroform, no dearylation occurs; an oxidative-reducing process takes place.

6. The behavior of triphenylbismuth resembles that of tetraethyllead, previously studied by one of the present authors [3]; this indicates that the strength of the Bi–C and Pb–C bonds is nearly equal.

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THE ACTION OF TRIETHYL PHOSPHITE AND DIETHYLSODIUM PHOSPHITE UPON SOME DIHALOGEN DERIVATIVES

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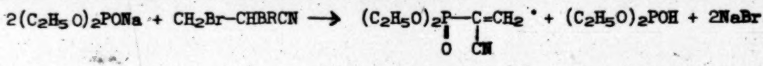
A.E.Arbuzov has shown that complete esters of phosphorous acid are isomerized to esters of alkyl phosphinic acids when reacted with alkyl halides [1]. He subsequently extended this reaction to the dihalogen derivatives of the paraffins. A.E.Arbuzov and N.P.Kushkova [2] synthesized the ethyl ester of iodomethylphosphinic acid by reacting triethyl phosphite with methylene iodide. They were unable to substitute a phosphono radical for the second atom of iodine. Nylen [3] reacted two molecules of diethylsodium phosphite with trimethylene bromide and secured the normal reaction product: an ester of trimethylenediphosphinic acid. This reaction was repeated by A.E.Arbuzov and N.P.Kushkova [2]. Nylen [3] reacted diethylsodium phosphite with ethylene bromide and secured ethylene as a reaction product. L.N.Parfentiev and M.Shafiev [4] reacted triethyl phosphite with trimethylene bromide and synthesized a γ-bromopropylphosphinic ester. G. Kosolapov [5] then reacted triethyl phosphite with ethylene bromide and did not get the corresponding esters of β-bromoethylphosphinic acid or an ester of ethanediphosphinic acid. On the other hand, one or both of the bromine atoms can be replaced by the phosphono group, as Kosolapoff's experiments [6] on the reaction of triethyl phosphite with trimethylene bromide have shown. In 1947, Ford-Moore and Williams [7] showed that it is easy to produce the tetraethyl ester of diphosphonomethane by reacting triethyl phosphite with methylene iodide. In this same research they succeeded in securing both the ethyl ester of β-bromoethylphosphinic acid and the tetraethyl ester of diphosphonoethane by reacting triethyl phosphite with ethylene bromide. In reacting the same triethyl phosphite with propylene bromide, Ford-Moore and Williams did not get the expected ester of β-bromopropylphosphinic acid (I), but a small quantity of an ester of propenylphosphinic acid (II), which was formed by the detaching of hydrogen bromide from the ester (I). The formation of the β-bromoethylphosphinic ester when triethyl phosphite is reacted with ethylene bromide was confirmed by Kosolapoff [8].

As this survey of the literature indicates, the reaction between complete esters of phosphorous acid or diethylsodium phosphite and the dihalogen derivatives of saturated hydrocarbons proceeds differently with the halogens in different positions. The singular behavior of the paraffin dihalogen derivatives in these reactions forced us to extend our experiments to other dihalogen derivatives as well.

We investigated the reaction of diethylsodium phosphite with α,β-dibromopropionitrile. Analysis of the reaction products indicated that the reaction involves the formation of the ethyl ester of phosphonoacrylonitrile and diethylphosphorous acid. Apparently, the primary product of the reaction between diethylsodium phosphite and α,β-dibromopropionitrile splits off hydrogen bromide, which reacts with diethylsodium phosphite to form free diethylphosphorous acid:

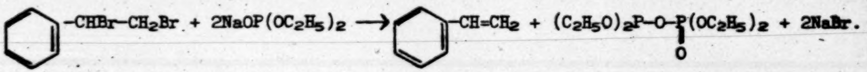


$$2(C_2H_5O)_2PONa + CH_2Br{-}CHBrCN \longrightarrow (C_2H_5O)_2\underset{O}{\underset{\|}{P}}{-}\underset{CN}{\underset{|}{C}}{=}CH_2{}^{*} + (C_2H_5O)_2POH + 2NaBr.$$

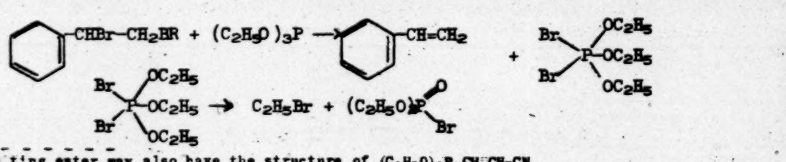
We were unable to secure the ester in the pure state by saponification. Hence, the reaction we have studied resembles the reaction of propylene bromide with triethyl phosphite, investigated by Ford-Moore and Williams.

It should be noted that we have found that the reaction between β-chloropropionitrile and diethylsodium phosphite proceeds normally, a high yield of the ethyl ester of β-phosphonopropiononitrile: $(C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}CH_2CH_2CN$ being secured. Saponification of the nitrile ester yielded β-phosphonopropionic acid with a m.p. of 166° [9].

The reaction of diethylsodium phosphite with dibromostyrene was entirely different. We might have expected, by analogy with the α,β-dibromopropionitrile, that this would result in the formation of an ester of styrylphosphinic acid. Experiment showed, however, that the principal reaction product was styrene, 53.7% of which was secured. After distillation of the complex mixture of phosphorus-containing fractions, the presence of an ester of subphosphoric acid was proved by producing the β-naphthylamide of the diethyl ester of phosphoric acid, with a m.p. of 69° (mixed test sample), by combining it with β-naphthyl amine. Thus, as was the case with dibromoethane, observed by Nylen [3], in this reaction the diethylsodium phosphite behaves like dissolved sodium, detaching the halogen from the dibromostyrene. The resulting phosphono radical undergoes complicated transformations and gives rise to a mixture of products, the chief of which is the tetraethyl ester of subphosphoric acid, as had been previously observed by A.E.Arbuzov and B.A.Arbuzov [10] when bromine was reacted with diethylsodium phosphite:



The fact that the action of styrene dibromide upon triethyl phosphite yields a similar result is quite interesting. When triethyl phosphite was reacted with dibromostyrene at 155-160°, ethyl bromide was produced. The reaction products included 50.2% (based on the dibromostyrene placed in the reaction) of styrene, together with a small quantity of diethylphosphorous acid and a complex mixture of organophosphorus derivatives, among which we demonstrated the presence of an ester of subphosphoric acid by forming the β-naphthyl amide of the diethyl ester of phosphoric acid, with a m.p. of 69°, by reacting the mixture with β-naphthyl amine [11]. Thus, the reaction of dibromostyrene with triethyl phosphite may be considered to proceed as follows:



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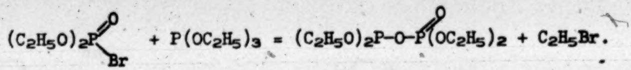
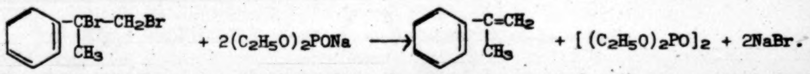
* The resulting ester may also have the structure of $(C_2H_5O)_2\underset{O}{\underset{\|}{P}}CH{=}CH{-}CN$



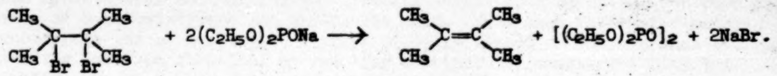
$$(C_2H_5O)_2P(O)Br + P(OC_2H_5)_3 = (C_2H_5O)_2P-O-P(O)(OC_2H_5)_2 + C_2H_5Br.$$

A reaction of this sort is quite conceivable, since Hall and Jacobson [12] have described the formation of tetraethyl pyrophosphate when triethyl phosphate was reacted with the acid chloride of diethylphosphoric acid. The formation of small amounts of diethylphosphorous acid is due to the partial cleavage of hydrogen bromide from the dibromostyrene under the experimental conditions. A special experiment was run to prove that dibromostyrene evolves hydrogen bromide at 155-170°. Reacted with triethyl phosphite, hydrogen bromide yields diethylphosphorous acid and ethyl bromide.

The reaction between diethylsodium phosphite and α-methylstyrene dibromide proceeds like the one involving dibromostyrene. In this case, the reaction products included 45.4% of α-methylstyrene:

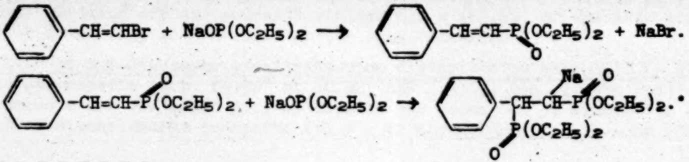


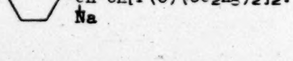
We might add that when diethylsodium phosphite is reacted with tetramethylethylene dibromide a high yield of tetramethylethylene is secured (this reaction has been studied by N. P. Bogonostseva):



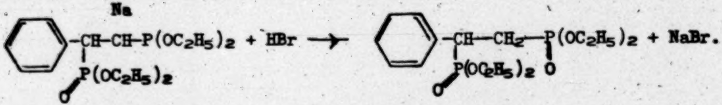
When styrene dibromide and α-methylstyrene are subjected to high temperature, hydrogen bromide may be split off, giving rise to ω-bromostyrene and ω-bromo-α-methylstyrene.

To ascertain the possibility of either ω-bromostyrene or ω-bromo-α-methylstyrene entering into reaction with triethyl phosphite or diethylsodium phosphite, we tested the action of diethylsodium phosphite and triethyl phosphite upon these bromides. The ω-bromostyrene reacts with diethylsodium phosphite only at high temperatures in a toluene medium. We were unable to secure the normal reaction product, the ethyl ester of ω-phosphonostyrene (the ester of styrylphosphinic acid). We secured 12% (based on the ω-bromostyrene placed in the reaction) of a high boiling product, the analysis of which corresponded to that of the tetraethyl ester of diphosphonophenylethane. Saponifying the latter yielded an acid with a m.p. of 212-214°, which proved upon analysis to be phenylethanediphosphinic acid. This result is not unexpected. As A.N.Pudovik and B.A.Arbuzov have shown [13], the action of diethylsodium phosphite upon the isomeric methoxychloropentenes results not only in the replacement of chlorine by the phosphono group, but also in the addition of the diethylsodium phosphite to the double bond, forming a diphosphono derivative. A similar reaction apparently occurs in the case of ω-bromostyrene. A molecule of diethylsodium phosphite is added to the ethyl ester of ω-phosphonostyrene initially formed. The resulting diphosphono derivative reacts with hydrogen bromide (which is detached from the ω-bromostyrene), giving rise to the free ester of diphosphonophenylethane.



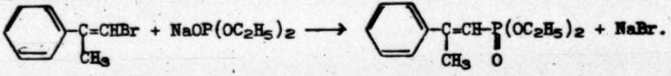
Or 

$$-CH(Na)-CH[P(O)(OC_2H_5)_2]_2.$$



We were unable to recover the products of the reaction of ω-bromostyrene with triethyl phosphite. No reaction occurs at high temperatures at ordinary pressure. Heating in a sealed tube results in the isomerization of the triethyl phosphite to the ethyl ester of ethylphosphinic acid.

The reaction of diethylsodium phosphite with α-methyl-ω-bromostyrene yielded small quantities (16%) of the ethyl ester of α-methyl-ω-phosphonostyrene. The reaction proceeds as follows:



As in the case of ω-bromostyrene, we were unable to isolate the diphosphono derivative in this instance either. Saponification of the ester of α-methyl-ω-phosphonostyrene with hydrochloric acid at 135-160° results in the opening of the P–C bond and the formation of α-methylstyrene and phosphoric acid. This same ester of α-methyl-ω-phosphonostyrene was produced with a yield of 33.5% (based on the α-methyl-ω-bromostyrene entering into the reaction) by reacting α-methyl-ω-bromostyrene with triethyl phosphite.

EXPERIMENTAL

Action of β-chloropropionitrile on diethylsodium phosphite. 28.5 g of β-chloropropionitrile (b.p. 63-65° at 10 mm; n_D^{20} 1.4370; d_{20}^{20} 1.1461) [14] was added drop by drop during the course of 30 minutes to an ether solution of diethylsodium phosphite, prepared from 44.2 g of diethylphosphorous acid (43.9 g required theoretically) and 7.2 g of metallic sodium in 450 ml of anhydrous ether. Sodium chloride was precipitated out. The contents of the flask were heated for one hour to the boiling point of ether (over a water bath). The sodium chloride was filtered out and washed with ether. A total of 17 g was obtained (18.3 g according to theory). The ether was driven off. The residue was vacuum distilled. Double distillation in vacuum yielded 42.7 g (70.2%) of the ethyl ester of β-phosphonopropionitrile, with a b.p. of 150-152° at 7 mm, as a colorless, water-soluble liquid, n_D^{20} 1.4380. For analytical purposes the substance was redistilled at 2 mm, b.p. 127-128°.

n_D^{20} 1.4380; d_{20}^{20} 1.1127.

0.0980 g substance. 27.04 ml NaOH ($\underline{T}$ = 0.02154). Found %: P 16.46.
$C_7H_{14}O_3NP$. Computed %: P 16.23.

Saponification. 9.9 g of the substance was heated with 30 ml of dilute hydrochloric acid (2:1) for 8 hours at 115-130° in a sealed tube. Repeated evaporation (over a water bath) yielded a solid colorless residue. The β-phosphonopropionic acid was extracted with anhydrous benzene and then with anhydrous acetone in a Soxhlet apparatus. Driving off the solvents yielded 6.2 g (78.5%) of the acid with a m.p. of 166°; a mixed test sample fused at the same temperature.

Action of α,β-dibromopropionitrile upon diethylsodium phosphite. 40.6 g of β-dibromopropionitrile (b.p. 89-90° at 10 mm; n_D^{20} 1.5390; d_{20}^{20} 2.0955 [15]) in 40 ml of anhydrous ether was added drop by drop in the course of 30 minutes to an ether solution of diethylsodium phosphite (53.3 g of diethylphosphorous acid [52.6 g ac-

according to theory] and 8.7 g of metallic sodium in 500 ml of anhydrous ether). Sodium bromide precipitated out. Suitable treatment resulted in the recovery of 30.2 g (78.7%) of anhydrous sodium bromide; 38.9 g are called for theoretically.

Repeated vacuum distillation yielded: 1) diethylphosphorous acid, with a b.p. of 60-65° at 7 mm; n_D^{20} 1.4080; d_{20}^{20} 1.0667; yield 7 g (11.9%); 2) the ethyl ester of phosphonoacrylonitrile, with a b.p. of 124-127° at 1 mm; n_D^{20} 1.4350; d_{20}^{20} 1.1277, as an oily liquid, readily soluble in water, decolorizing bromine water and a potassoum permanganate solution instantaneously. Yield 9.5 g (26.4%).

> 0.0847 g substance: 24.13 ml NaOH (T = 0.02148). Found %: P 16.94.
> $C_7H_{12}O_3NP$. Computed %: P 16.40.

Saponification. 6.4 g of the substance was heated to 150-165° for 10 hours in a sealed tube with 30 ml of dilute hydrochloric acid (1:1). Repeated evaporation until all the HCl had been eliminated yielded 5.3 g of a solid, contaminated with a thick liquid. Extraction with alcohol (rendered anhydrous with CaO) yielded 0.52 g (29%) of ammonium chloride; elimination of the alcohol yielded 4 g of a thick liquid that contained minute quantities of a crystalline product. Heating this with barium carbonate produced a mixture of Ba salts. Fractional recrystallization from water isolated 0.6 g of a barium salt that was insoluble in water. Analysis indicated that it was barium phosphonoacrylate, $C_6H_4P_2O_{10}Ba_3$, or barium phosphate, $BaHPO_4$.

> 0.4388 g of the Ba salt*: 0.4312 g $BaSO_4$; Found: Ba 0.2538 g.
> $C_6H_4P_2O_{10}Ba_3$. Computed: Ba 0.2547 g. $BaHPO_4$. Computed: Ba 0.2581 g.

Large quantities, as much as 3.2 g, of a soluble barium salt were recovered. According to its barium content, the formula of this barium salt approximates $C_6H_8O_{10}P_2Ba$.

> 0.7342 g Ba salt : 0.4324 g $BaSO_4$. Found Ba 0.2545 g. $C_6H_8O_{10}P_2Ba$.
> Computed: Ba 0.2295.

Action of α,β-dibromopropionitrile upon triethyl phosphite. 32.8 g of triethyl (31.5 g called for theoretically) was added drop by drop during the course of 30 minutes to 20.2 g of dibromopropionitrile. The temperature was raised from 16° to 87° and was kept in the 87-99° range (within the reaction mixture) while the ethyl bromide was driven off. Toward the end of the reaction the flask contents were heated to 150° for 15 minutes. This yielded 19 g (20.6 called for by theory) of ethyl bromide, with a b.p. of 38-40°. Yield 92.2%. We were unable to isolate individual products despite repeated vacuum distillation.

Action of ω-bromostyrene upon diethylsodium phosphite. 16.1 g of ω-bromostyrene (b.p. 88-90° at 10 mm; n_D^{20} 1.6018; d_{20}^{20} 1.4094) was poured into a toluene solution of diethylsodium phosphite (13.1 g of diethylphosphoric acid [12.1 g called for theoretically] and 2 g of metallic sodium in 100 ml of anhydrous toluene). No sodium bromide settled out. Sodium bromide was precipitated when the toluene was boiled**; this heating lasted 4 hours. Suitable treatment yielded 6.6 g (9 g called for theoretically) of anhydrous sodium bromide. The reaction product was distilled in vacuum, first at 10 mm, with the high-boiling fraction distilled at 1 mm. A total of 7.1 g (44%) of the original ω-bromostyrene (b.p. 213-220°; n_D^{20} 1.5850; d_{20}^{20} 1.3673) was recovered after repeated distillations and a preliminary treatment of the corresponding fraction with water. After redistillation the b.p. was 213-215°; n_D^{20} 1.5938; d_{20}^{20} 1.3947. The first vacuum distillation of the high-boiling fraction yielded 1.9 g of the ethyl ester of diphosphonostyrene (b.p. 181° at 1 mm; n_D^{20} 1.4920; d_{20}^{20} 1.1524) as a thick, water-soluble liquid. Yield 12.0% (based on the diethylsodium used for the reaction).

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* After desiccation to constant weight in a revolving exsiccator at 100°.

** Sodium bromide did not separate out from the ethyl ether solution

0.0730 g substance: 22.24 ml NaOH (T = 0.01928). Found %: P 16.27.
$C_{16}H_{28}O_6P_2$. Computed %: P 16.40.

Saponification. 0.8 g of the substance was heated to 120-130° in a sealed tube for 7 hours with 10 ml of diluted hydrochloric acid (1:1). The solution was treated with ether, and 0.1 g of an oily liquid was extracted. Repeated evaporation yielded 0.5 g (0.56 g called for theoretically) of diphosphonostyrene as colorless crystals, readily soluble in water and alcohol, with a m.p. of 212-214°. Heating the aqueous solution with activated charcoal and then evaporating the solution yielded an acid with the same melting point.

0.0514 g substance[*]: 21.60 ml NaOH (T = 0.01928). Found %: P 22.43.
$C_8H_{12}O_6P_2$. Computed %: P 23.30.

Action of ω-bromostyrene on triethyl phosphite. 14.5 g of triethyl phosphite was slowly added drop by drop, during the course of an hour, to 14.9 g of the bromostyrene heated to 200-210°, which caused the phosphite to distil over. 12.7 g of triethyl phosphite was distilled; no ethyl bromide was driven off when the mixture was heated over a water bath (to 80°). The distilled triethyl phosphite was poured into a reaction flask. The original substance was distilled in vacuum (10 mm) with a minute residue.

Repetition of the experiment. 26.2 g of triethyl phosphite and 14.5 g of ω-bromostyrene were heated to 180-200° for 8 hours in a sealed tube. The initial ω-bromostyrene and the ethyl ester of ethylphosphinic acid, plus a negligible residue, were recovered by distillation in vacuum (12 mm).

Action of styrene dibromide (C_6H_5-CHBr-CH_2Br) on diethylsodium phosphite. An ether solution of 34.6 g of styrene dibromide (m.p. 72°) in 80 ml of anhydrous ether was added during the course of 35 minutes to an ether solution of diethylsodium phosphite (37.5 g of diethylphosphorous acid [36.1 g called for theoretically] and 6 g of metallic sodium in 500 ml of anhydrous ether). Sodium bromide precipitated out. The mixture was heated for 2 hours to the point where the ether boiled. After the usual treatment the reaction product was distilled in vacuum (11 mm): Fraction I - b.p. 43-90°, a colorless liquid, weight 18.3 g; Fraction II - b.p. 90-132°, a colorless liquid, weighing 14.4 g, containing colorless crystals. The residue was a thick liquid containing a crystalline substance. After cooling, 0.8 g of the original dibromide, with a m.p. of 70°, was recovered. The filtrate was combined with Fraction II.

Analysis of Fraction I. (b.p. 43-90° at 11 mm). 50 ml of water was added to the fraction (18.3 g); the undissolved product (9.5 g), with the odor of styrene, was treated in the cold with bromine in chloroform solution. This yielded 16 g of styrene dibromide with a m.p. of 72-73° (mixed test sample = 72°), corresponding to 6.3 g of styrene or 53.7% (based on the styrene dibromide used in the reaction). The portion of the fraction that dissolved in the water is apparently diethylphosphorous acid.

Analysis of Fraction II (b.p. 90-132° at 11 mm). Repeated vacuum distillation yielded: 1) 4 g of the original styrene dibromide with a m.p. of 70-71°, i.e. the total styrene dibromide recovered was 4.8 g; 29.8 g (86.1% entered in the reaction; 2) after a preliminary removal of the original styrene dibromide by vigorous chilling, the action of β-naphthyl amide upon the fraction with a b.p. of 105-130° at 3 mm yielded 1.2 g of the β-naphthyl amide of diethylphosphoric acid, with a m.p. of 69° (mixed test sample), which corresponds to 1.18 g of the ethyl ester of subphosphoric acid, or 3.85% (based on the styrene dibromide used in the reaction). No ethyl ester of ω-phosphonostyrene or diphosphonostyrene was recovered.

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[*] The ester and the acid of diphosphonostyrene require prolonged heating (as much as 80 hours) with periodic additions of nitric acid (sp.gr. 1.5). They were analyzed after drying at 100° in a revolving exsiccator.

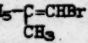
Action of styrene dibromide on triethyl phosphite. 22 g of triethyl phosphite (20.1 g called for theoretically) was added drop by drop during the course of an hour to 16 g of styrene dibromide heated to 155-160°, driving off ethyl bromide (none of it distilled over up to 150°). The heating was continued for one hour at 165-170°. This yielded 8.6 g (11.8 g called for by the theory) of ethyl bromide with a b.p. of 38-40°.

The reaction product was distilled in vacuum: Fraction I – b.p. 54-74° at 15 mm, a colorless liquid, weight 13.6 g; Fraction II – b.p. 103-157° at 2 mm, a colorless liquid, weight 10.3 g, residue – 1.7 g of an amorphous solid product.

Analysis of Fraction I (b.p. 54-74° at 15 mm). Redistillation at 11 mm yielded the following fractions: I) b.p. 45-65°, weight 4.7 g. A colorless liquid with the odor of styrene. Bromination resulted in the production of 7.2 g of styrene dibromide with a m.p. of 71-72° (mixed test sample 71°), which corresponds to 28.3 g of styrene, or 50.2% (based on the styrene dibromide used for the reaction); II) b.p. 69-72°; n_D^{20} 1.4116; d_{20}^{20} 1.0627; weight 3.8 g. Impure diethylphosphorous acid. All of the fraction dissolved in water. The Beilstein reaction was negative.

Analysis of Fraction II (b.p. 103-157° at 2 mm). Redistillation yielded the following fractions: I) up to 117° at 2 mm. This fraction yielded a total of 1.7 g of the original styrene dibromide with a m.p. of 71-72°; II) b.p. 117-131° at 2 mm. After preliminary recovery of the original styrene dibromide by chilling, treatment of this fraction with β-naphthyl amine yielded 0.8 g of the β-naphthyl amide of diethylphosphoric acid, with a m.p. of 69°, which corresponds to 0.7 g of the ethyl ester of subphosphoric acid, or 4.8% (based on the styrene dibromide used for the reaction). Neither the ethyl ester of ω-phosphonostyrene nor diphosphonostyrene was recovered. When styrene dibromide was heated with triethyl phosphite to 155-170° in a separate test, under the same experimental conditions, large quantities of hydrogen bromide were evolved, which explains the formation of diethylphosphorous acid. No styrene was found.

Action of diethylphosphorous acid upon styrene dibromide. 10.2 g of diethylphosphorous acid was added drop by drop during the course of 30 minutes to 9.2 g of styrene dibromide heated to 195-205°, causing ethyl bromide to be driven off (no C_2H_5Br is evolved up to 190°). Heating was continued for 1 hour at 210-215°. 4.1 g of ethyl bromide (with a b.p. of 38-39°) was driven off. After the ethyl bromide had been driven off, the residue, which weighed 1.5 g and smelled like styrene, was treated with a chloroform solution of bromine. This yielded 0.7 g of styrene dibromide with a m.p. of 70-71°, which corresponds to 0.27 g or 7.5% of styrene.

Action of α-methyl-ω-bromostyrene  $(C_6H_5-\underset{CH_3}{C}=CHBr)$ on diethylsodium phosphite. An ether solution of 21.4 g of α-methyl-ω-bromostyrene (b.p. 103-105° at 11 mm; n_D^{20} 1.5880; d_{20}^{20} 1.3790 [16]) in 20 ml of anhydrous ether was added drop by drop to an ether solution of diethylsodium phosphite (16 g of diethylphosphorous acid [15 g called for by theory] and 2.5 g of metallic sodium in 200 ml of anhydrous ether). Sodium bromide precipitated out. The mixture was heated for 1 hour while the ether boiled. Suitable treatment yielded 8.4 g of anhydrous sodium bromide (85.7%), based on the α-methyl-ω-bromostyrene used in the reaction).

A second vacuum distillation yielded: 1) 2.1 g of the original α-methyl-ω-bromostyrene with a b.p. of 95-98° at 9 mm; n_D^{20} 1.5680; 19.3 g (90%)of the bromide entered into the reaction; and 2) the ethyl ester of α-methyl-ω-phosphonostyrene with a b.p. of 146-149° at 1 mm (n_D^{20} 1.5210; d_{20}^{20} 1.1094) as an oily liquid that is insoluble in water and instantaneously decolorized a chloroform solution of bromine. Yield 4 g, or 16% (based on the α-methyl-ω-bromostyrene used for the reaction).

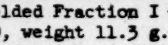
0.0828 g substance: 18.7 ml NaOH (T = 0.01928). Found %: P 12.06.
$C_{13}H_{19}O_3P$. Computed %: P 12.20.

Saponification. 1.4 g of the substance was heated with 12 ml of dilute hydrochloric acid (1:1) for 6 hours to 135-145° and for 4 hours to 145-160° in a sealed tube. After the ethyl chloride had been evaporated, the surface of the solution exhibited an oily layer, constituting contaminated α-methylstyrene,[*] weight 0.5 g. Repeated evaporation over a water bath to remove all the HCl yielded a thick liquid (phosphoric acid); when this was reacted with phenylhydrazine in alcoholic solution, we obtained 1.5 g of phenylhydrazine phosphate; m.p. 155° after recrystallization from alcohol (a mixed test sample fused at the same temperature).

Action of α-methyl-ω-bromostyrene of triethyl phosphite. 12.5 g of triethyl phosphite (11.4 g called for by theory) was added drop by drop during the course of 40 minutes to 13.6 g of methylbromostyrene heated to 150-160°, ethyl bromide being driven off (no C_2H_5Br was driven off up to 150°). Heating was continued for 1 hour at 165-170°. 2.3 g (36.5% of the theoretical) of ethyl bromide was distilled. Repeated vacuum distillations yielded: 1) 2.1 g of the original α-methyl-ω-bromostyrene; n_D^{20} 1.5358; d_{20}^{20} 1.2668; with a b.p. of 208-210° (this fraction was treated with water before distillation); 2) 3.1 g of diethylphosphorous acid with a b.p. of 65-80° at 10 mm (part of the fraction dissolved in water during treatment); and 3) 5 g of the ethyl ester of α-methyl-ω-phosphonostyrene, with a b.p. of 149-150° at 1.5 mm; n_D^{20} 1.5190; d_{20}^{20} 1.1009, or 33.5% (based on the α-methyl-ω-bromostyrene used for the reaction).

0.0796 g substance: 18.8 ml NaOH (T = 0.01928). Found %: P 12.61.
$C_{13}H_{19}O_3P$. Computed %: P 12.20.

Saponification. 3.3 g of the substance was heated with 20 g of dilute hydrochloric acid (1:1) in a sealed tube for 10 hours at 120-130°. The upper layer yielded 1.7 g of contaminated α-methylstyrene after the ethyl chloride had been evaporated. Repeated evaporation of the aqueous solution to eliminate all the HCl yielded a thick liquid - phosphoric acid. When this was reacted with phenylhydrazine, we secured 3.7 g of phenylhydrazine phosphate. The m.p. was 154-155° after recrystallization from alcohol; a mixed test sample fused at the same temperature.

Action of α-methylstyrene dibromide ( $C_6H_5-\underset{CH_3}{CBr}-CH_2Br$) on diethylsodium phosphite. An ether solution of 30.6 g of α-methylstyrene dibromide [prepared with 13 g of α-methylstyrene (b.p. 163°; d_{20}^{20} 0.9098) dissolved in 300 ml of anhydrous ether, to which 17.6 g of bromine was added during the course of 1.5 hours while the mixture was chilled with snow] is added during the course of an hour to an ether solution of diethylsodium phosphite [33 g of diethylphosphorous acid (30.3 g called for by theory) and 5.3 g of metallic sodium in 400 ml of anhydrous ether]. Sodium bromide was precipitated out. The contents of the flask were heated for 2 hours while the ether boiled. Repeated vacuum distillation yielded Fraction I - b.p. 41-43° at 3 mm, a colorless liquid; n_D^{20} 1.4867; d_{20}^{20} 0.9750, weight 11.3 g. Treatment with water yielded 5.9 g (45.4%) of α-methylstyrene with a b.p. of 160-162°; d_{20}^{20} 0.9201. The portion of the fraction that dissolved is apparently diethylphosphorous acid. We were unable to secure any individual compounds from the higher fractions.

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[*] With an unsharp boiling point. Similar results were obtained when α methylstyrene was heated in a sealed tube for 10 hours to 120-130° with dilute hydrochloric acid (1:1) - the conditions for the experiment with triethyl phosphite.

SUMMARY

1. The action of diethylsodium phosphite and triethyl phosphite upon various dibromides has been investigated. It has been shown that the reaction is different for dibromides of different structure.

2. The action of diethylsodium phosphite upon α,β-dibromopropionitrile yielded the ethyl ester of phosphonoacrylonitrile.

3. With styrene dibromide and α-methylstyrene dibromide, the action of diethylsodium phosphite results in the formation of styrene and α-methylstyrene. The reaction between tetramethylethylene dibromide and diethylsodium phosphite is similar, resulting in the formation of tetramethylethylene. Triethyl phosphite acts upon styrene dibromide similarly to diethylsodium phosphite, detaching bromine and forming styrene.

4. The reaction of ω-bromostyrene with diethylsodium phosphite is singular, involving the attachment of another molecule of diethylsodium phosphite at the double bond and the formation of the tetraethyl ester of diphosphonophenylethane.

In the case of α-methyl-ω-bromostyrene, reaction with diethylsodium phosphite yielded only the ethyl ester of α-methyl-ω-phosphonostyrene.

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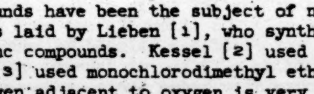
STERIC HINDRANCES IN ORGANOMAGNESIUM REACTIONS

X. THE SINGULAR COURSE OF THE REACTION BETWEEN α-MONOCHLOROSUBSTITUTED ETHERS AND ARYL MAGNESIUM HALIDES. (A NEW METHOD OF SYNTHESIZING STERICALLY COMPLEX SYMMETRICAL DIARYL ETHANE HYDROCARBONS)

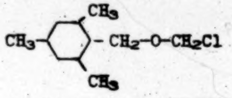
I. I. Lapkin and O. M. Lapkina

The problems involved in the synthesis of ether by reacting halogen ethers with organometallic compounds have been the subject of numerous researches. The foundation for this research was laid by Lieben [1], who synthesized an ether by reacting halogen ethers with organozinc compounds. Kessel [2] used dichlorodiethyl ether for this reaction, while Henry [3] used monochlorodimethyl ether. These researches established the fact that a halogen adjacent to oxygen is very readily replaced by the hydrocarbon group of an organometallic compound. Hamonet [4,5] was the first to employ organomagnesium compounds instead of organozinc compounds in synthesizing ethers by this reaction. Further researches proved that ethers of the most varied types can be synthesized by reactions of organomagnesium compounds with halogen ethers [6-10]. An unsymmetrical dihalogen-substituted ether likewise proved suitable for this purpose. In this case the chlorine atom in the α-position reacts [11-13]. Tseltner and Tarasov [14], as well as Pavlovsky [15], found that in contrast to unsymmetrical halogen-substituted ethers, both chlorine atoms react readily in a symmetrical halogen-substituted methyl ether.

The research we undertook on the effect of the structure of organomagnesium compounds upon the course of their reactions with halogen ethers began with a study of the reaction between mesitylmagnesium bromide and a symmetrical dichlorodimethyl ether. This reaction proceeds normally, i.e., the sole reaction product is 2,4,6,2',4',6'-hexamethyl benzyl ether, with a yield of 45% (Experiment 1).

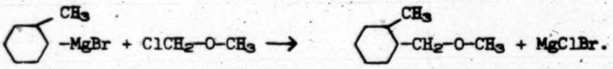


Endeavors to arrest this reaction at its first stage, i.e., the stage in which the compound

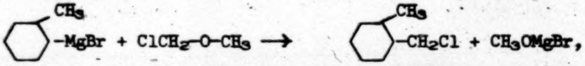


is formed, have met with failure thus far.

The reactions of aryl magnesium halides with α-monochloro-substituted ethers yielded differing results, depending upon the degree of substitution of the alkyl groups in the ortho positions. Mono-ortho-substituted aryl magnesium halides react with these ethers normally, giving rise to the corresponding ethers. o-Tolylmagnesium bromide, for example, reacts with monochlorodimethyl ether to form methyl-2-methyl benzyl ether (Experiment 2).

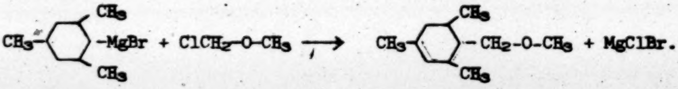


Though the rather intense lachrymatory properties of the product, which persist even after it has been carefully freed of traces of monochlorodimethyl ether by fractionation indicate the possibility that the reaction may take another course:



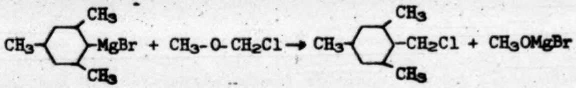
if this does occur, it does so in a quite insignificant degree, inasmuch as practically no NaCl is isolated from the alcoholic solution when it is treated with sodium methylate. α-Naphthylmagnesium bromide reacts in the same manner with monochlorodimethyl ether. The reaction product is methyl-α-naphthyl methyl ether (Experiment 3). The reaction of monochloromethyl ethyl ether with α-naphthylmagnesium bromide introduces nothing new into the chemistry of organometallic compounds. Ethyl-α-naphthyl methyl ester is the sole reaction product (Experiment 4). This new factor is observed only in reactions of diortho-substituted aryl magnesium halides with the same α-chloro-substituted ethers.

When mesitylmagnesium bromide is reacted with monochlorodimethyl ether, one of the reaction products is methyl-2,4,6-trimethyl benzyl ether (Experiment 5).



The substance formed possesses lachrymatory properties, which do not disappear after prolonged refining by fractionation. When it is purified with sodium methylate in a solution of methanol, an extensive precipitate of NaCl is thrown down, after which the lachrymatory property of the product vanishes, it then consisting of pure methyl-2,4,6-trimethyl benzyl ether. When the product is treated with sodium isoamylate, a certain amount of isoamyl-2,4,6-trimethylbenzyl ether is formed.

All this indicates that the reaction follows another course as well, namely, the formation of 2,4,6-trimethylbenzyl chloride:



which is contained in the same fraction as the methyl-2,4,6-trimethyl benzyl ether, owing to the closeness of their boiling points.

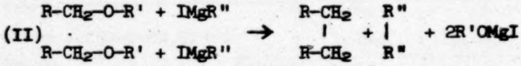
Analysis of the product obtained in the foregoing reaction indicates that it consists of methyl-2,4,6-trimethyl benzyl ether (42%) and 2,4,6-trimethylbenzyl chloride (58%) (cf Experiment 5). The existence of this second course of the reaction is also indicated by the fact that the reaction of mesitylmagnesium bromide with monochlorodimethyl ether in the presence of an excess of magnesium yields symmetrical dimesitylethane, the formation of which may be explained as due to Wurtz reactions:

$$R\text{-}CH_2Cl + Mg \longrightarrow R\text{-}CH_2MgCl.$$

$$R\text{-}CH_2MgCl + ClCH_2R \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}R + MgCl_2.$$

This concept of the formation of dimesitylethane may be countered, however, by objections based upon the results of the researches of G.Stadnikov and V.Chelintsev. As we know, the ability of ethers to resist the action of organomagnesium compounds depends upon the nature of the radicals attached to the ether oxygen. The more uniform the electrochemical nature of these radicals, the more stable the ether. The aliphatic ethers, which contain primary radicals, are cleaved only at high temperature, according to the researches of Spath [16]. The aliphatic-aromatic ethers break down at lower temperatures when acted upon by organomagnesium compounds, according to Grignard [17,18], and Simonis and Remmert [19]. Later, Stadnikov discovered that ethers of the $C_6H_5CH_2\text{-}O\text{-}CH_2R$ type (where R is an alkyl) react rather easily with alkyl magnesium halides [20]. V. Chelintsev and Pavlov [21] assume that this reaction takes place according to Equation (I) or (II):

$$\text{(I)}\quad R\text{-}CH_2\text{-}O\text{-}R' + IMgR'' \rightarrow R\text{-}CH_2\text{-}R'' + R'\text{-}O\text{-}MgI$$



$$\text{(II)}\quad \begin{matrix} R\text{-}CH_2\text{-}O\text{-}R' + IMgR'' \\ R\text{-}CH_2\text{-}O\text{-}R' + IMgR'' \end{matrix} \rightarrow \begin{matrix} R\text{-}CH_2 \\ | \\ R\text{-}CH_2 \end{matrix} + \begin{matrix} R'' \\ | \\ R'' \end{matrix} + 2R'OMgI$$

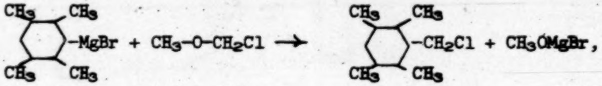
It seemed that the researches of Stadnikov and Chelintsev opened up the possibility of another explanation of the reaction involving the formation of dimesitylethane, namely, in accordance with the foregoing Equation (II), but the absence of dimesityl among the reaction products was a counter-indication against this possibility. Moreover, if dimesitylethane were formed in accordance with the equation proposed by Chelintsev and Pavlov, it would have been noticed, no matter whether it took place with an excess of magnesium present or not, whereas the explanation of the synthesis of dimesitylmethane based upon Wurtz-type reactions requires the presence of excess magnesium.

Special tests (Experiment 5) that were run to carry out this reaction with excess magnesium present (an ether solution of monochlorodimethyl ether was added to an ether solution of mesitylmagnesium bromide in the presence of an excess of magnesium) and with no such excess present (the solution of mesitylmagnesium bromide in ether was separated from the excess of magnesium and then added to the ether solution of monochlorodimethyl ether) resulted in the formation of dimesitylethane, together with the other specified products, in the first case, with no such product formed in the second case. Although we repeated the foregoing tests several times, these results remained unchanged: dimesitylethane was produced when residual magnesium was present, but none of this hydrocarbon was found when no residual magnesium was present. This circumstance finally confirms the singular nature of the reaction between mesitylmagnesium bromide and monochlorodimethyl ether, which results in the formation of methyl-2,4,6-trimethyl benzyl ether and 2,4,6-trimethylbenzyl chloride, as set forth above, together with dimesitylethane as the product of further transformation of the chloride when residual magnesium is present.

The cause of this dual course of the reaction must be sought in the fact that when the ortho effect of the phenyl radicals is intensified, groups begin to react that are less active but are more accessible sterically owing to their smaller molecular volume, (the atomic distance between C and OCH_3 is 1.45 Å, and between C and Cl is 1.71 Å).

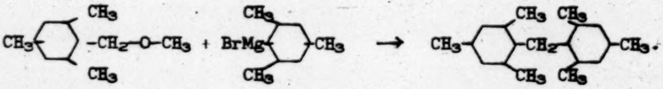
This singularity of the reaction between mesitylmagnesium bromide and monochlorodimethyl ether may be employed to develop a method of synthesizing (symmetrical) dimesitylethane. Since this reaction yields 42% of the ether and 58% of the chloride (when carried out with no residual magnesium present), all the chloride may be converted into a diaryl ethane by changing the reaction conditions slightly. All that is required is the addition of activated magnesium after the reagents (the organomagnesium compound and the α-chloroether) have been mixed together, and heating the mixture for some time (Experiment 6).

The reaction of mesitylmagnesium bromide with monochloromethyl ether (Experiment 7) is similar to that between mesitylmagnesium bromide and monochlorodimethyl ether. It was to be expected that the intensification of the ortho effect, the accessibility of the chloromethyl group to the point of reaction, would be lowered still more, and that only the methoxy group of the monochlorodimethyl ether would react. This possibility is confirmed by the reaction between duryl magnesium bromide and the same monochlorodimethyl ether. In the duryl radical, the ortho effect is greater than in the mesityl radical, owing to the presence of two methyl groups in the meta positions, which repel the methyl groups located at the ortho positions. As a result, the principal reaction product is 2,3,5,6-tetramethylbenzylchloride (Experiment 8):



which can be converted into symmetrical didurylethane by changing the experimental conditions as set forth above.

Experiment 9 was set up to ascertain the feasibility of synthesizing hydrocarbons of the diaryl methane type by reacting sterically complicated ethers with diortho-substituted organomagnesium compounds according to the following equation:



When the Grignard reagent is present in excess and the reaction mixture is heated for a long time (10 hours) to the boiling point of the xylene solution, the corresponding diaryl methane is formed with a yield of approximately 20%.

EXPERIMENTAL

1. Reaction of mesitylmagnesium bromide with dichlorodimethyl ether. Initial substances: 50 g (0.25 mol) of bromomesitylene, 7 g of magnesium, and 14.5 g (0.125 mol) of dichlorodimethyl ether. An ether solution of the dichlorodimethyl ether was added drop by drop, with mechanical stirring and chilling, to an ether solution of

mesitylmagnesium bromide. The reaction mixture was heated for 7 hours and then decomposed with water and 10% hydrochloric acid. Decomposition yielded an abundant white precipitate, which was filtered out, washed with water, desiccated, and recrystallized from petroleum ether. After having been twice recrystallized, the product was sublimed in vacuum for final purification, after which it exhibited a constant melting point of 146-147° (2,4,6,2',4',6'-hexamethyl dibenzyl ether).

0.1189 g substance; 0.3718 g CO_2, 0.0989 g H_2O. Found %: C 85.33; H 9.31: $C_{20}H_{26}O$. Computed %: C 85.10; H 9.28.

After the precipitate had been removed, the ether layer was separated from the aqueous one in the usual manner, washed with a 10% soda solution and then with water until its reaction was neutral. After the ether had been driven off, some more 2,4,6-2',4',6'-hexamethyl dibenzyl ether was recovered; this was purified in the same manner as the bulk of the product. A total of 16 g (45%) of the ether was secured. This ether is not described in the chemical literature.

2. Reaction of o-tolylmagnesium bromide with monochlorodimethyl ether. Initial substances: 81 g (0.5 mol) of o-bromotoluene, 13 g of magnesium, and 40 g (0.5 mol) of monochlorodimethyl ether. The sequence in which the reagents were mixed was the usual one. The ether solution of monochlorodimethyl ether was added to the chilled ether solution of o-tolylmagnesium bromide. The reaction mass was heated for 3 hours. The resulting reaction products were distilled in vacuum. The following fractions were recovered at 30 mm: I – up to 70°, II – 70-120°, weight 48 g; residue, weight 3 g. Redistillation yielded 40 g (51%) of a product with a b.p. of 95-96° at 30 mm, which was further refined by heating it with sodium methylate dissolved in methanol. No NaCl settled out. After purification the substance had a b.p. of 97° at 32 mm (methyl-2-methyl benzyl ether).

d_4^{20} 0.9777; n_D^{20} 1.5040, MR_D 41.21; Computed MR_D 41.89.
0.1056 g substance: 0.3065 g CO_2, 0.0846 g H_2O. Found %: C 79.22; H 8.97. $C_9H_{12}O$. Computed %: C 79.42; H 8.85.

3. Reaction of α-naphthylmagnesium bromide with monochlorodimethyl ether. Initial substances: 104 g of α-bromonaphthalene (0.5 mol), 13 g of magnesium and 40 g (0.5 mol) of monochlorodimethyl ether. The reaction conditions were the same as in the preceding experiment. The following fractions were secured at 8 mm: I – up to 130°; II – 130-140°, weight 51 g; and III – 250-270°, weight 10 g. Fraction II was redistilled. This yielded 47 g (55%) of methyl-α-naphthyl methyl ether, with a b.p. of 106-107° at 3 mm. The boiling point of the ether did not change after it was purified by heating it with sodium methylate dissolved in methanol.

d_4^{20} 1.0830; n_D^{20} 1.6037; MR_D 54.60; computed MR_D 52.52;
exaltation (^{E}M) of the naphthalene ring approximately 2 [22].

0.1222 g substance: 0.3741 g CO_2; 0.0764 g H_2O: 0.2130 g substance: 0.2663 g AgI. Found %: C 83.54, H 7.00; OCH_3 16.5. $C_{12}H_{12}O$. Computed %: C 83.69; H 7.02; OCH_3 18.0.

The b.p. given for this ether in the literature is 101-103° at 1.5 mm [23].

Fraction III contained no α,β-di-(naphthyl-1)-ethane. We were unable to determine the nature of the substances that comprised Fraction III.

4. Reaction of α-naphthylmagnesium bromide with monochloromethyl ethyl ether. Initial substances: 42 g (0.2 mol) of α-bromonaphthalene, 6 g of magnesium, and 19 g (0.2 mol) of monochloromethyl ethyl ether. The reaction conditions were the same as in the two preceding experiments. The reaction mixture was heated for 5 hours. The following fractions were secured at 5 mm: I – up to 120°; II – 120-140°, weight 24 g; residue, weight 5 g. Redistillation of Fraction II yielded 20 g (54%) of ethyl-α-naphthyl dimethyl ether, with a b.p. of 115-116° at 3 mm. The boiling point did not

change after purification with sodium ethylate dissolved in ethyl alcohol.

d_4^{20} 1.1001; n_D^{20} 1.6076; MR_D 58.50; Computed MR_D 57.14.

0.1172 g substance: 0.3591 g CO_2; 0.0801 g H_2O. 0.1362 g substance: 0.1643 g AgI. Found %: C 83.61; H 7.65; OC_2H_5 23.0. $C_{13}H_{14}O$. Computed %: C 83.84, H 7.57; OC_2H_5 24.2.

The b.p. of this ether is given as 144° at 11 mm in the literature [32].

5. Reaction of mesitylmagnesium bromide with monochlorodimethyl ether. The following quantities were used for this reaction: 100 g (0.5 mol) of bromomesitylene, 14 g of magnesium, and 40 g (0.5 mol) of monochlorodimethyl ether. The monochlorodimethyl ether, dissolved in ether, was gradually added, with ice-chilling and mechanical stirring, to an ether solution of mesitylmagnesium bromide. The reaction mixture was heated for 7 hours over a water bath and then decomposed with water and 10% hydrochloric acid. The ether was driven off from the washed and desiccated ether solution and the mixture of products remaining within the flask was distilled in vacuum. The following fractions were secured at 3.5 mm: I – up to 85°; II – 85-130°, weight 46.0 g; III – 130-190°, weight 6.0 g; residue, weight 2.0 g. Fractionation of Fraction II yielded 40 g of a product with a b.p. of 90-107° at 5 mm. When this substance was heated with sodium methylate dissolved in methanol, a precipitate of NaCl settled out. After purification, the resulting methyl-2,4,6-trimethylbenzyl ether had a b.p. of 93-94° at 6 mm; d_4^{20} 0.9484; n_D^{20} 1.5100; MR_D 51.71; Computed MR_D 51.04.

To prove the presence of a methoxy group in the resulting ether, a small quantity of the substance was heated with hydriodic acid, as prescribed by Feist [24]; the methyl iodide that was formed was carried by a current of CO_2 to an absorption tube filled with a 10% alcoholic solution of dimethylaniline. This yielded trimethylphenylammonium iodide with a m.p. of 210-211° (from alcohol). The m.p. given for this substance in the literature is 211-212° [25] (according to Zeisel).

0.1206 g substance: 0.1554 g AgI. Found %: OCH_3 17.1. $C_{11}H_{16}O$. Found %: OCH_3 18.9.

The b.p. given in the literature for this ether is 109-110° at 15 mm [33]. The 130-190° (at 3.5 mm) fraction was redistilled and then recrystallized from petroleum ether (b.p. 70-90°). This yielded a finely crystalline substance with a m.p. of 117-118° (symmetrical dimesitylethane). Yield 9%. The m.p. given for this hydrocarbon in the literature [28] is 117-118°.

Found %: C 90.08; H 10.05. $C_{20}H_{26}$. Computed %: C 90.16; H 9.84.

Another test was run with the same quantities of reagents, but mixing them in the inverse order. The prepared ether solution of mesitylmagnesium bromide was combined with an excess of magnesium and gradually poured, with chilling and constant stirring, into an ether solution of the monochlorodimethyl ether. Finally, the mixture was heated for 7 hours and decomposed in the usual manner. The principal resulting fraction, with a b.p. of 90-107° at 5 mm (44 g), was analyzed to determine the percentage of 2,4,6-trimethylbenzyl chloride in it (a weighed batch of the product was treated with an alcoholic solution of ammoniacal silver nitrate that had been saturated while hot) [24] as well as its percentage of methyl-2,4,6-trimethylbenzyl ether (by the number of methoxy groups):

0.4786 g substance: 0.2378 g AgCl: Found %: Cl 12.29.

The product contained 58% of 2,4,6-trimethylbenzyl chloride.

0.1402 g substance: 0.0842 g AgI. Found %: OCH_3 7.94.

The product contained 42% of methyl-2,4,6-trimethyl benzyl ether. The rest of the product (the 90-107° [5 mm] fraction, weighing 42 g) was heated with sodium isoamylate dissolved in isoamyl alcohol. The abundant precipitate of NaCl that settled out was filtered out and washed with ether. This yielded 8 g of NaCl, which confirms the presence of 2,4,6-trimethylbenzyl chloride in the quantity specified above. After the NaCl had been removed, the filtrate was washed with water until its reaction was neutral, desiccated with anhydrous sodium sulfate, and subjected to double fractionation in vacuum. In addition to the methyl-2,4,6-trimethylbenzyl ether, we secured isoamyl-2,4,6-trimethylbenzyl ether, with a b.p. of 127-128° at 6 mm:

d_4^{20} 0.9115; n_D^{20} 1.4950; MR_D 70.38; Computed MR_D 69.51.

0.1958 g substance: 0.5853 g CO_2; 0.1897 g H_2O. Found %: C 81.57; H 10.84. $C_{15}H_{24}O$. Computed %: C 81.76; H 10.98.

No symmetrical dimesitylethane is formed in this experiment.

6. Synthesis of dimesitylethane. This experiment was also set up under somewhat different conditions in order to convert all the 2,4,6-trimethylbenzylchloride formed in the reaction between mesitylmagnesium bromide and monochlorodimethyl ether into symmetrical dimesitylethane. An ether solution of mesitylmagnesium bromide, prepared from 40 g (0.2 mol) of bromomesitylene and 7 g of magnesium was mixed with an excess of magnesium and added, as in the preceding experiment, to an ether solution of 16 g (0.2 mol) of monochlorodimethyl ether. Then 2 molar % of $CuCl_2$ was added to the reaction mixture, followed by 2 g of well-activated magnesium. Adequate activation is attained by adding 1-2 ml of ethyl bromide to the magnesium covered with a layer of sulfuric ether, and then, after a vigorous reaction has set in, decanting the ether solution from the magnesium. When Mg is added, the reaction mixture usually heats up to boiling. Finally, the mixture was heated for 5 hours and decomposed, as usual, with a 10% solution of acetic acid. Fractionation of the resulting product in vacuum at 4 mm yielded the following fractions: I - up to 80°; II - 80-120°, weight 6.0 g; III - 150-200°, weight 8.7 g; residue, weight 1.0 g. Redistillation of Frac-III yielded 7.0 g of a product boiling within a narrower range (170-173° at 4 mm), which was then purified by double recrystallization from petroleum ether. The melting point of the synthesized symm dimesitylethane was 117-118°. The yield was 24%, based on the bromomesitylene. In view of the percentage yield of the 2,4,6-trimethylbenzyl chloride established in the preceding experiment, as well as of the fact that Fraction II contains no chloride, it may be stated that all the chloride is converted into dimesitylethane under these experimental conditions.

7. Reaction of mesitylmagnesium bromide with monochloromethyl ether. Initial substances: 40 g (0.2 mol) bromomesitylene, 7 g of magnesium, and 19 g (0.2 mol) of monochloromethyl ethyl ether. The reaction conditions were the same as in Experiment 2. The following fractions were recovered at 4 mm: I - up to 95°; II - 95-145°, weight 16 g; III - 145-190°, weight 3.5 g; residue, weight 2 g. Fraction II was redistilled and purified by heating it with sodium ethylate dissolved in absolute ethyl alcohol. This yielded 10 g of ethyl-2,4,6-trimethylbenzyl ether, with a b.p. of 89-90° at 2.5 mm.

0.1011 g substance: 0.2986 g CO_2; 0.0932 g H_2O. 0.1410 g substance: 0.1780 g AgI. Found %: C 80.60; H 10.31; OC_2H_5 24.2. $C_{12}H_{18}O$. Computed %: C 80.85; H 10.18. OC_2H_5 25.6.

According to the literature [33], this ether boils at 114-115° at 14 mm.

The 145-190° (4 mm) fraction was redistilled and then recrystallized from petroleum ether. This yielded symm. dimesitylethane with a m.p. of 117-118°.

8. Reaction of durylmagnesium bromide with monochlorodimethyl ether. Usually bromodurene reacts with magnesium only in the presence of ethyl bromide [28,29], 30.4 g

(1/7 mol) of bromodurene, 16g (1/7 mol) of ethyl bromide and 9g of Mg were taken for preparing durylmagnesium bromide. The prepared ether solution of the mixture of organomagnesium compounds was decanted from the residual magnesium and poured, with chilling and mechanical stirring, into an ether solution of 23 g of monochlorodimethyl ether. The reaction mixture was heated for 6 hours and then decomposed with water and 10% acetic acid. The aqueous layer was separated, and the ether layer was washed with a soda solution and with water and then desiccated with calcined sodium sulfate. The mixture of products that remained after the ether had been driven off over a water bath was fractionated in vacuum. The following fractions were recovered at 6 mm: I – up to 120°; II – 120-130°, weight 8.0 g; residue, weight 1.0 g. The products in Fraction II contained neither OH nor OCH_3 groups; their percentage of active chlorine as determined by a saturated alcoholic solution of ammoniacal silver nitrate, was 12.86%, indicating that the fraction contained 66% of 2,3,5,6-tetramethylbenzyl chloride. Hence, no methyl-2,3,5,6-tetramethylbenzyl ether is formed in this reaction, nothing but the chloride being formed.

A second experiment in our study of this reaction was set up with the same quantities of reagents, but with the conditions slightly changed so as to produce symmetrical didurylethane. The reaction was carried out with residual magnesium present; as a result, the 2,3,5,6-tetramethylbenzyl chloride formed at first in a Wurtz reaction was converted into symm. didurylethane. An ether solution of monochlorodimethyl ether was added with chilling and constant stirring, to a prepared ether solution of durylmagnesium bromide without separating the latter from its excess magnesium. The reaction mixture was heated for 6 hours and then decomposed in the usual manner. As water and acetic acid were added, a white precipitate was seen to settle out; it was filtered out, washed with soda, and desiccated. This yielded 3.5 g of an anhydrous substance, which was purified by recrystallizing it from toluene until its melting point was constant at 234-235°. The output of pure symmetrical didurylethane [1,2-bis-(2,3,5,6-tetramethylphenyl)-ethane] was 2.1 g (10% based on the bromodurene used in the reaction).

0.1102 g substance: 0.3615 g CO_2; 0.1012 g H_2O. Found %: C 89.61; H 10.27; $C_{22}H_{30}$. Computed %: C 89.73; H 10.27.

According to Fuson [27], the m.p. of symmetrical didurylethane is 235-236°.

9. Reaction of mesitylmagnesium bromide with methyl-2,4,6-trimethyl benzyl ether (at a high temperature). Initial substances: 50 g (0.25 mol) of bromomesitylene, 7 g of magnesium, and 20.5 g (0.125 mol) of methyl-2,4,6-trimethyl benzyl ether. A xylene solution of the methyl-2,4,6-trimethyl benzyl ether was added to an ether solution of mesitylmagnesium bromide. The mixture was first heated to 100° over a water bath (to drive off the ether) and then over a bath of Wood's metal for 10 hours at the boiling point of the xylene solution. After the excess mesitylmagnesium bromide that had not entered the reaction had been decomposed and the xylene had been driven off, the residual mixture was distilled in vacuum. Redistillation of the major fraction, with a b.p. of 140-190° at 8 mm, yielded 8 g of a fraction that distilled within a narrower range (154-156° at 2 mm); it was further purified by recrystallization from petroleum ether. This yielded 6 g of pure dimesitylmethane, with a m.p. of 132-133°. Yield 20%.

0.1058 g substance: 0.3498 g CO_2; 0.0915 g H_2O. Found %: C 90.23; H 9.68. $C_{19}H_{24}$. Computed %. C 90.41; H 9.59.

The m.p. of dimesitylmethane is given in the literature [30,31] as 130, 134, and 135°. No dimesitylethane was detected in the reaction products.

SUMMARY

1. The reaction of monoortho-substituted aryl magnesium halides and monochlorodi-

methyl or monochloromethyl ethyl ether takes place normally and results in the formation of ethers of the $R-CH_2-O-CH_3$ and $R-CH_2-O-C_2H_5$ type.

2. When this same reaction is carried out between diortho-substituted aryl magnesium halides and the specified halogen ethers, it follows two courses: ethers of the same type are formed plus, to a large extent, ortho-substituted benzyl chlorides. When this reaction is carried out with a large enough amount of excess magnesium, all the chloride is converted into a hydrocarbon of the symm. diaryl ethane type. This method is recommended for the preparation of hydrocarbons of this type.

3. Symmetrical α-dichloro-substituted ethers (dichlorodimethyl ether) react normally with both the monoortho- and the diortho-substituted aryl magnesium halides, i.e., they form ethers of the $R-CH_2-O-CH_2R$ type.

4. Methyl-2,4,6-trimethyl benzyl ether reacts with mesitylmagnesium bromide only at high temperature (140-150°). Dimesitylmethane is formed under these conditions.

5. Some ethers hitherto unknown in the chemical literature have been synthesized and described.

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STERIC HINDRANCES IN ORGANOMAGNESIUM REACTIONS

XI. REACTIONS OF FORMATES WITH ORGANOMAGNESIUM COMPOUNDS

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The reactions of organomagnesium compounds with formates are rather varied.

As we know from the researches of A. Zaitsev, E.Wagner, and I.Kannonikov and M. Zaitsev [1,2,3], organozinc compounds react with formates to form secondary alcohols. Composite organomagnesium compounds react similarly with the formates, as has been established by Grignard [4].

But, in his very first investigation of this reaction, Grignard found a deparure from the usual course of this reaction, namely, the formation of formates instead of the expected secondary alcohols Stadnikov [5] demonstrated that the presence of such a discrepancy is due to an exchange reaction between the resulting halogen magnesium carbinolates and the initial esters. Subsequent researches established that still another departure from the normal course of this reaction is possible. Schmidlin and Massini [6] made a study of the reaction of ethyl formate with α-naphthylmagnesium bromide and found that in one of their experiments ethyl-α,α-dinaphthylmethyl ether was formed with a quantitative yield. This same anomaly was observed by Stadnikov [5]. Favorsky and Kolotova [7] found still another anomaly of this reaction. When they reacted ethyl formate with tert-butylmagnesium chloride, they secured tert-butylcarbinol instead of the expected di-tert-butylcarbinol. Lastly, changing the ratio of the reagents may result in still another product, namely, an aldehyde [8].

The different products secured in the foregoing reaction indicate that this reaction is extremely sensitive to changes in the external conditions. This sensitivity is due to the high mobility of the hydroxyl group in compounds of the tri- and dicarbinol type; it may be the cause of still other departures from the ordinary course of this reaction. We encountered one such new anomaly in a study of the reaction between ethyl formate and ortho-substituted aryl magnesium halides. As has been said in previous papers by one of the present authors [9,10], diaryl methanes were produced in this reaction instead of the expected diaryl carbinols. The present research, undertaken with a view to further investigation of this reaction, has shown that the appearance of such anomalies depends upon the presence of metallic impurities in the magnesium.

Two samples of metallic magnesium were used in our study of the reaction of ethyl formate with ortho-substituted aryl magnesium halides. When the first sample was used, the reaction usually resulted in the formation of hydrocarbons of the diaryl methane type, while the second sample yielded a mixture of a diaryl carbinol and a diaryl methane in the same reaction. When mesitylmagnesium bromide (prepared from the first sample of magnesium) is reacted with ethyl formate (2:1), the principal reaction product formed is dimesitylmethane, as had already been pointed out in our previous papers [9,10]. Carrying out this reaction with the second sample of magnesium, however, results in the formation of a mixture of dimesitylcarbinol and dimesitylmethane (Experiment 1). To eliminate the factor of chance, these experiments were repeated several times, but their results remained unchanged. These results forced us to conclude that both magnesium samples contain traces of other metals, which change the course of the reaction. There are more of these impurities in the first sample than in the second. Similar observations on the effect of impurities in the magnesium upon the results of reactions involving organomagnesium compounds had been often made at an earlier date. This circumstance is stressed in a series of papers by Kharasch and his associates [11,12,13]. These researches indicated that traces of other metals in commercial magnesium, and the halogen derivatives formed from them in the course of the reaction, can change the trend of the reaction. Cobalt chloride exerts the greatest effect. Upon the assumption that the anomalous trend of the reaction of mesitylmagnesium bromide with ethyl formate when the first magnesium sample was used, and to some extent when the second sample was used, is due to causes of this sort, i.e., the catalytic effect of some metal halides upon the reaction, we set up supplementary experiments to study this reaction using catalystst: cobalt chloride ($CoCl_2$) and cuprous chloride (Cu_2Cl_2). The results of these tests confirmed the correctness of our hypotheses. When mesitylmagnesium bromide, prepared from the purer second sample of magnesium, was reacted with ethyl formate in the presence of 2 molar % of cobalt chloride, the only reaction product was dimesitylmethane. It should also be noted that the reactions which result in the production of dimesitylmethane also exhibit the formation of somewhat larger quantities of high-boiling products than in other experiments, the nature of which we were unable to ascertain. Other results are obtained when cuprous chloride is used as the catalyst. When mesitylmagnesium bromide, prepared as before, from the purer second sample of magnesium, is reacted with ethyl formate, it forms a mixture consisting of dimesitylcarbinol and dimesitylmethane, in about the same amounts as when no catalyst is present. The existence of the above-mentioned anomaly was confirmed by one of the present authors [9,10] in the reactions of ethyl formate with other diortho-substituted aryl magnesium halides. These reactions were carried out with no cobalt chloride present, but with magnesium that was less pure (Sample 1). The following fact should be mentioned: in the reactions of diorthosubstituted aryl magnesium halides with formates that result in the formation of diaryl methanes, a pink (or red) color is evident, which disappears after a brief interval of time. Lastly, the reactions of ethyl formate with those monoorthosubstituted aryl magnesium halides that have a branched alkyl group at the ortho position also result in the formation of hydrocarbons of the diaryl methane series. 3-Cymylmagnesium bromide, for example, prepared from the less pure, first sample of magnesium, likewise forms a hydrocarbon – di-(3-cymyl)-methane – instead of a secondary alcohol when reacted with ethyl formate (Experiment 2). The results change only when we shift to the aryl magnesium halides that cause only negligible steric hindrances or none at all. In these cases no color appears in the solution when the formate is added to the organomagnesium compound, and the reaction results in the usual product of this reaction – a secondary alcohol.

The corresponding diaryl carbinols are formed when o-tolylmagnesium, p-tolylmagnesium, and α-naphthylmagnesium bromides, prepared from both of the magnesium samples used by us, are reacted with ethyl formate. Carrying out these reactions in the presence of cobalt chloride does not affect the results.

Hence, the effect of impurities (including $CoCl_2$) in metallic magnesium is felt only in the reactions of ethyl formate with diorthosubstituted aryl magnesium halides and in reactions with monosubstituted halides that have branched radicals in the ortho position, i.e., in those reactions which proceed slowly because of steric inhibitions; they do not affect rapid reactions. Kharasch [11] points out that when $CoCl_2$ is present, the trend of the reaction depends upon the rate at which the hypothetical complex organocobalt compound (RCOCl) is decomposed. If this rate is small compared to the rate at which the Grignard reagent is added to the ketone, the reaction follows a normal course, and a carbinol is formed; when the converse is true, a pinacol is formed. This variation of the trend of the reaction with its velocity is even more readily seen in the reactions studied by us, since the trend of the reaction depends solely upon the degree of steric inhibition, for the identical chemical nature of the radicals in the organometallic compounds.

As for the mechanism of this anomalous reaction, it is as yet impossible to clear up the details of this problem without supplementary research, without thorough investigation of the nature of the high-boiling fractions, which we have been unable to do as yet in certain instances; without this information any judgment concerning the mechanism of this reaction would be too general in its nature.

EXPERIMENTAL

I. Reaction of mesitylmagnesium bromide with ethyl formate (2:1 ratio). [1]The conditions under which ethyl formate was reacted with the mesitylmagnesium bromide prepared from the first, less pure, sample of magnesium, yielding dimesitylmethane, have been described in detail in our Report I [9]. We reacted ethyl formate (0.125 mol) with mesitylmagnesium bromide prepared from bromomesitylene (0.25 mol) and the second, purer sample of magnesium, under the same reaction conditions. The reaction product was distilled in vacuum. The following fractions were collected at 7 mm: I – up to 160°; II – 160-260°, weight 10.5 g; residue, weight 2 g. Fraction II, which proved to be a mixture of dimesitylcarbinol and dimesitylmethane, crystallized at once. This mixture was separated by means of the differing solubilities of its constituents in petroleum ether (b.p. 70-90°). The whole mixture of crystals was transferred into 10 times its weight of petroleum ether. When heated, one part of the crystals (a) dissolved more readily than the other part (b), and was thus separated. When this solution was left to stand at room temperature, crystals separated out which proved to have a constant m.p. of 148-149° after subsequent recrystallizations from the same solvent (dimesitylcarbinol or 2,4,6,2',4',6'-hexamethylbenzohydrol).

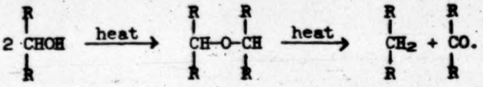
0.1123 g substance: 0.3512 g CO_2; 0.0934 g H_2O. 0.1120 g substance: 10.2 ml CH_4 (18°, 730 mm). Found %: C 85.34; H 9.31; OH 6.24. $C_{19}H_{24}O$. Computed %: C 85.03; H 9.01; OH 6.34.

The m.p. given for dimesitylcarbinol in the literature [14,15] are 147-148° and 150°. Chilling the mother liquor with ice caused crystals to settle out; they were purified by recrystallization from petroleum ether. M.p. 133-134° (dimesitylmethane).

0.1124 g substance: 0.3719 g CO_2; 0.0955 g H_2O. Found %: C 90.30; H 9.55. $C_{19}H_{24}$. Computed %: C 90.41; H 9.59.

A test sample exhibited the same melting point when mixed with dimesitylmethane produced by another method [16]. The crystals (b) that did not dissolve in the petroleum ether were caused to dissolve by heating them in a fairly large quantity of the same solvent. When the solution was cooled, a crystalline substance with the m.p. of 140-146° settled out. After further recrystallizations this substance (dimesitylcarbinol) exhibited a m.p. of 148-150°. A test sample exhibited no depression of the melting point when mixed with the previously synthesized crystals of dimesitylcarbinol. The experiment resulted in the preparation in the pure state of

4 g of dimesitylcarbinol and 1 g of dimesitylmethane. When this experiment was carried out, the reaction products were distilled in vacuum, as indicated above, so that it might be expected that the dimesitylmethane was formed during the process of distillation as follows:



$$2\,\underset{R}{\overset{R}{\mathrm{CHOH}}} \xrightarrow{\text{heat}} \underset{R}{\overset{R}{\mathrm{CH}}}\!-\!\mathrm{O}\!-\!\underset{R}{\overset{R}{\mathrm{CH}}} \xrightarrow{\text{heat}} \underset{R}{\overset{R}{\mathrm{CH_2}}} + \underset{R}{\overset{R}{\mathrm{CO}}}.$$

Though dimesitylcarbinol proves to be a stable substance in this respect, distilling at 205° at 8 mm with decomposition, after which its melting point remains constant at 149-150°, this hypothesis compelled us to repeat this experiment, excluding the operation of heating the reaction mixture as well as the vacuum distillation of the reaction products. After the ether had been expelled, the reaction products were chilled in a freezing mixture; the crystals that settled out were separated from the liquor and recrystallized repeatedly from petroleum ether (80-90° fraction), after which they exhibited a constant m.p. of 148-149° (dimesitylcarbinol). The substance in the liquor was dissolved in petroleum ether (fraction up to 70°) and then chilled; this yielded crystals that were purified by repeated recrystallization from the same solvent. The melting point – 132-133° – and the fact that no depression of the melting point occurred when a test sample was mixed with the crystals produced previously indicate that this substance is dimesitylmethane. As a result of this test we secured 5 g of dimesitylcarbinol and 2.5 g of dimesitylmethane in the pure state from the reaction products.

2. The following experiment on the reaction of mesitylmagnesium bromide with ethyl formate was run with the same quantities of reagents, but 2 molar % of $CoCl_2$ was placed in the reaction flask containing the organomagnesium compound before the reagents were mixed together. After heating for half an hour, the second component (ethyl formate) was added to the flask, and the reaction mixture was heated for 5 hours. As in the preceding experiments, the solution turned pink when the second component was added. The reaction products were distilled in vacuum. The major fraction (150-210° at 8 mm) crystallized at once, and two recrystallizations were required to secure pure dimesitylmethane with a constant m.p. of 132-133°. No dimesitylcarbinol was found.

> 0.1026 g substance: 0.3391 g CO_2; 0.0888 g H_2O. Found %: C 90.19; H 9.63. $C_{19}H_{24}$. Computed %: C 90.41; H 9.59.

II. Reaction of 3-cymylmagnesium bromide with ethyl formate (2:1 ratio). Initial substances: 42 g (0.12 mol) of 3-bromocymene, 7.5 g (0.125 mol) of ethyl formate, and 6.5 g of magnesium (first, less pure sample). The reaction of these substances was carried out under the usual conditions. The product obtained after the ether had been driven off was distilled in vacuum. The following fractions were collected at 10 mm: I – up to 140°, weight 9 g; II – 140-240°, weight 11 g; residue, weight 4 g. Fraction II was redistilled. Two fractions were collected, with b.p. of 200-230° and 230-250° at 12 mm. The fraction with a b.p. of 230-250° at 12 mm crystallized and was purified by recrystallizing it from petroleum ether. This yielded di-3-cymylmethane with a m.p. of 222°.

> 0.1074 g substance: 0.3557 g CO_2; 0.0948 g H_2O. Found %: C 90.38. H 9.88. $C_{21}H_{28}$. Computed %: C 89.94; H 10.05.

The 200-230° (12 mm) fraction was a liquid mixture of products, the true nature of which we were unable to determine, though we were able to recover some additional di-3-cymylmethane with a m.p. of 222° by treating the mixture with alcoholic caustic potash and then subjecting it to a Clemmensen reduction. Some 4 g of the pure hydrocarbon was secured in all.

III. Reaction of o-tolylmagnesium bromide with ethyl formate. Initial substances: 42.8 g (0.25 mol) of o-bromotoluene, 6 g of magnesium (second, purer sample) and 9.3 g (0.125 mol) of ethyl formate. The reaction conditions were the usual ones. After the ether had been expelled, the reaction product was chilled with ice and salt. The crystals of di-o-tolylcarbinol that settled out were filtered out of the liquor and recrystallized from petroleum ether (fraction below 70°) until its m.p. was constant at 119-120°.

0.1220 g substance; 0.3798 g CO_2; 0.0782 g H_2O. 0.1167 g substance: 13.2 ml CH_4 (18°, 730 mm). Found %: C 84.95; H 7.69; OH 7.73. $C_{15}H_{16}O$. Computed %: C 84.87; H 7.59; OH 8.01.

The m.p. given in the literature for this compound is 119.5° [16]. The yield of the pure product was 5 g. The liquid portion of the reaction product was distilled in vacuum. This yielded the following fractions at 8 mm: I – 130-190°, weight 6 g; II – 190-280°, weight 9 g; residue, weight 4 g. Another 2 g of pure di-o-tolylcarbinol was recovered from Fraction I. The 190-280° (8 mm) fraction yielded 5 g of a narrower fraction (265-267° at 7 mm), which crystallized only after long standing, once it had been dissolved in petroleum ether. Further recrystallizations from the same solvent mixed with toluene (4:1) yielded the crystals of symmetrical tetra-o-tolylethane with a m.p. of 253-254°.

0.0364 g substance: 0.1229 g CO_2; 0.0254 g H_2O. Found %: C 92.18; H 7.80. $C_{30}H_{30}$. Computed %: C 92.26; H 7.74.

According to the literature [17], the m.p. of this hydrocarbon is 257°. The yield of the 190-280° (8 mm) fraction is increased to 14 g by heating the reaction mixture for 10 hours. The results of the experiment were not affected by adding cobalt chloride (0.7 g).

IV. Reaction of p-tolylmagnesium bromide and ethyl formate. Initial substances: 42.8 g (0.25 mol) of p-bromotoluene, 9.3 g of ethyl formate, and 6.5 g of magnesium (second, purer sample). The reaction conditions were the usual ones. The mixture of reaction products was chilled with ice after the ether had been driven off. The crude cyrstalline product that settled out weighed 10.5 g after it had been separated from the liquor. Recrystallization from petroleum ether yielded di-p-tolylcarbinol, with a m.p. of 69-70°.

0.1265 g substance: 0.3933 g CO_2; 0.0839 g H_2O. 0.1239 g substance: 14.8 ml CH_4 (18°, 730 mm). Found %: C 84.84; H 7.42; OH 8.14. $C_{15}H_{16}O$. Computed %: C 84.87; H 7.59; OH 8.01.

The m.p. of p-tolylcarbinol is given as 69° in the literature [18]. The liquid portion of the reaction product was distilled in vacuum. This yielded: Fraction I – up to 165° at 7 mm, weight 1.5 g; Fraction II – 165-290° at 9 mm, weight 3.4 g; residue, weight 2 g.

Fraction I crystallized. Recrystallization from petroleum ether yielded p,p-ditolyl with a m.p. of 119-120°.

0.1043 g substance: 0.3525 g CO_2; 0.0753 g H_2O. Found %: C 92.23; H 8.07. $C_{14}H_{14}$. Computed %: C 92.25; H 7.75.

The m.p. given for this hydrocarbon in the literature is 120°. Fraction II also crystallized. This crystalline substance does not dissolve in petroleum ether, but it is soluble in a large quantity of boiling toluene. M.p. 276-277° (symmetrical tetra-p-tolylethane).

0.1129 g substance: 0.3819 g CO_2; 0.0809 g H_2O. 0.0645 g substance: 0.2179 g CO_2; 0.0458 g H_2O. Found %: C 92.30, 92.20; H 8.01, 7.95. $C_{30}H_{30}$. Computed %: C 92.26; H 7.74.

Bachman [19] gives 278-279° as the m.p. of this hydrocarbon.

Another experiment was run to try out this reaction when a catalyst – cobalt chloride – was used. The major reaction product was di-p-tolylcarbinol. We were unable to detect any di-p-tolylmethane.

V. We do not think it is necessary to describe the reaction of α-naphthylmagnesium bromide with ethyl formate, inasmuch as it has been described twice [20,8]. In our experiments we always secured di-α-naphthylcarbinol as the principal reaction product, with α,α-dinaphthyl methyl ether as the by-product. Adding cobalt chloride introduced no changes into the course of the reaction.

SUMMARY

1. The trend of the reaction between aryl magnesium halides and ethyl formate depends upon the traces of metals in the magnesium. The influence of the impurities is felt most strongly in reactions of the diorthosubstituted aryl magnesium halides, as well as in the reactions of the monoorthosubstituted halides that possess branched radicals at the ortho position, i.e., in the reactions that proceed slowly because of steric inhibitions. In these cases, diaryl methanes are formed instead of the usual products – diaryl carbinols. The impurities do not affect fast reactions.

2. Cobalt chloride has the same effect upon the trend of this reaction.

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THE REDUCTION OF β-(ALKOXY AROYL)-PROPIONIC ACIDS AND THE SYNTHESIS OF γ-(ALKOXY ARYL)-BUTYROLACTONES

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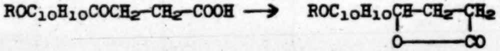
The objective of the present research is the synthesis of compounds with the lactone ring outside the aromatic portion of the tetrahydronaphthalene group. The initial substances we used were β-[1-alkoxy-(6,7,8)-tetrahydronaphthoyl-4)-propionic acids [1,2]. The butyrolactones:



$$\mathrm{ROC_{10}H_{10}COCH_2{-}CH_2{-}COOH} \longrightarrow \mathrm{ROC_{10}H_{10}}\begin{array}{l}\mathrm{CH{-}CH_2{-}CH_2}\\ \mathrm{O{-}{-}{-}{-}{-}CO}\end{array}$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_7H_{15}, were readily synthesized by reducing these acids with sodium amalgam and then heating the reaction products with a mineral acid.

In view of the fact that the yields of the butyrolactones were negligible, we investigated the catalytic reduction of these keto acids with Raney's alloy. Papa, Schwenk, and Whitman [3] have investigated the reduction of the carbonyl group by means of Raney's alloy; these authors found that the redution of compounds possessing a carbonyl group directly attached to a carbon atom in the aromatic ring yields hydrocarbons; in a compound whose carbonyl group is not attached directly to a ring carbon atom, the carbonyl group is reduced only to a secondary alcohol group. It therefore seemed to be more likely that in our case the employment of Raney's alloy would result in the formation of alkoxytetrahydronaphthylbutyric acids, rather than alkoxytetrahydronaphthylhydroxybutyric acids. We found, however, that compounds of this type do not obey the rules laid down by the researchers mentioned above. Whenever Raney's alloy was used, the carbonyl group was reduced only to a secondary alcohol group, inasmuch as heating the reaction product with a mineral acid yielded the corresponding butyrolactones. No depression of the melting point was observed in a mixed test sample of the lactones produced by reduction with sodium amalgam and with Raney's alloy.

Since the results of our experiments did not agree with the figures cited by Papa, Schwenk, and Whitman, we effected a Clemmensen reduction of β-[1-alkoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acids and obtained the corresponding γ-[1-alkoxy-(5,6,7,8)-tetrahydronaphthyl-4]-butyric acids in order to provide a further check of our results. Determinations of the melting point of test samples of the substances produced by a Clemmensen reduction, mixed with corresponding lactones produced by reduction with Raney's alloy, always exhibited a depression. The discrepancy between our results and the results cited by the foregoing authors may be attributed to the effect of the carboxyl group or of the tetrahydronaphthalene group. To learn whether this trend of the reaction applies to γ-keto acids with other aromatic rings, we subjected similar keto acids, in the naphthalene as well as in the benzene series, to reduction with Raney's alloy. This reaction was carried out with 2-ethoxy- and 2-propoxynaphthoyl-6-propionic acids and with p-methoxybenzoylpropionic acid. In the first case, the compounds recovered were identical with the lactones synthesized by means of sodium amalgam; in the second case, the resulting compound corresponded to the lactone synthesized by Rosenmund and Shapiro [4] as the result of the catalytic reduction of p-methoxybenzoylpropionic acid with palladium. Thus, it may be stated that the presence of a carboxyl group exerts a retarding effect upon the reduction of γ-alkoxy aryl keto acids with Raney's alloy. The table gives the melting points of the γ-alkoxy aryl butyrolactones synthesized by various methods, as well as the melting points of some γ-alkoxy aryl butyric acids and those of mixed test samples.

Keto acid	Melting points of lactones synthesized by reduction			Melting points of corresponding alkoxy butyric acids	Melting points of mixed test samples of the butyric acids and the corresponding lactones
	With sodium amalgam	With Raney's alloy	m.p. of mixed test samples		
1-Ethoxytetrahydronaphthoyl-4-propionic acid	93-94°	95-97°	94-97°	107-110	-
1-Methoxytetrahydronaphthoyl-4-propionic acid	121-123	122-124	121-124	122-123	100-106°
1-Butoxytetrahydronaphthoyl-4-propionic acid	83-87	84-87	84-87	90-92	70-77
1-Hexoxytetrahydronaphthoyl-4-propionic acid	81-82.5	81-83	80-83	[*]	-
2-Ethoxynaphthoyl-6-propionic acid.	125-126	125-126	125-126	[**]	-
2-Propoxynaphthoyl-6-propionic acid.	127.5-129	128-129	128-129	119.5-120.5[***]	-
p-Methoxybenzoylpropionic acid...	-	52-54	-	63-64	-

As for the advantages of the method of reducing γ-alkoxy aryl keto acids by means of Raney's alloy over the method of reduction involving the use of sodium amalgam, it must be pointed out that we were able to raise the lactone yield from 30 to 70% for the simplest alkoxy keto acids (methoxy, ethoxy) of the tetrahydronaphthalene series. The lactone yield drops considerably as the size of the radical in the alkoxy group is increased; this holds true for sodium amalgam reduction as well as for reduction with Raney's alloy. The reduction method involving the use of Raney's alloy did not yield good results in the synthesis of a lactone with a free hydroxy group attached to the ring; the lactone was synthesized only when sodium amalgam was used.

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[*] Not synthesized

[**] Not synthesized

[***] Melting points of 2 propoxynaphthoyl 6- and p-methoxyphenylbutyric acids taken from the literature.

EXPERIMENTAL

1. The Lactone of [1-Ethoxy-(5,6,7,8)-tetrahydronaphthyl-4-]-hydroxybutyric Acid.

a) Reduction of β-[1-ethoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with 20% sodium amalgam. 30 g of 20% sodium amalgam was added gradually, with mechanical stirring, during the course of 9-10 hours to 3 g of β-[1-ethoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 193-196°, dissolved in 50 ml of 10% Na_2CO_3. The reaction was carried out at room temperature, from 5 to 10 ml of water being added from time to time. The reaction mass was separated from the layer of mercury. The precipitate was suction-filtered and then washed several times with ether to remove the vaseline oil; an aqueous suspension was prepared, which was acidulated with 10% hydrochloric acid until its Congo reaction was acid and then boiled over a screen for 10-15 minutes. The resultant lactone was extracted with ether. The ether extract was washed with 3% sodium bicarbonate and with water and then desiccated with sodium sulfate. After the ether had been driven off until the residual volume was small, the precipitate was filtered out and washed several times with small batches of ether. Recrystallization from alcohol to which charcoal had been added yielded 0.9 g of a substance (32% of the theoretical). The lactone of [1-ethoxy-5,6,7,8)-tetrahydronaphthyl-4]-hydroxybutyric acid consists of colorless, lustrous crystals with a m.p. of 93-94° which are insoluble in water and readily soluble in organic solvents.

3.421 mg substance: 9.251 mg CO_2; 2.420 mg H_2O. 3.580 mg substance: 9.700 mg CO_2; 2.489 mg H_2O. Found %: C 73.75; 73.90; H 7.91, 7.78. $C_{16}H_{20}O_3$. Computed %: C 73.84; H 7.69.

b) Reduction of β-[1-ethoxy-(5,6,7,8]-tetrahydronaphthoyl-4]-propionic acid with Raney's alloy. 10 g of β-[1-ethoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 192-195°, was dissolved in 300 ml of 10% KOH; 30 g of Raney's alloy was gradually added, with mechanical stirring, to this solution, heated to 80-90°. Heating and stirring were continued for another hour after the alloy had been added. Then the catalyst was filtered out while hot. The catalyst was washed several times with hot water. The aqueous solutions were acidulated with dilute hydrochloric acid. A voluminous precipitate settled out; the reaction mixture was heated over a screen until drops of a thick oil appeared. The oil hardened upon cooling; it was comminuted and dissolved in ether. The ether solution was washed with 3% sodium bicarbonate and with water and then dried with sodium sulfate. The ether was driven off to small volume. The deposit that formed was filtered out and washed repeatedly with small batches of alcohol. This yielded 7.5 g of a substance with a m.p. of 88-92°. Recrystallization from alcohol and charcoal yielded 6.5 g of colorless, lustrous crystals with a m.p. of 95-97°, the yield being 70% of the theoretical. A test sample of this lactone, mixed with the lactone with a m.p. of 93-94° previous prepared by reduction with sodium amalgam, fused at 94-97°.

5.870 mg substance: 15.862 mg CO_2; 4.005 mg H_2O. Found %: C 73.69; H 7.63. $C_{16}H_{20}O_3$. Computed %: C 73.84; H 7.69.

The same methods were used for carrying out the reaction and treating the reaction products that have been described in detail in the experiments on the synthesis of 1-ethoxy-(5,6,7,8)-tetrahydronaphthyl-4-butyrolactone.

2. The Lactone of [1-Methoxy-(5,6,7,8)-tetrahydronaphthyl-4)-hydroxybutyric Acid*

a) Reduction of β-[1-methoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with

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[*] This lactone was synthesized by A. Burger [5] by catalytically reducing the methyl ester of methoxynaphthoylpropionic acid with a chromium catalyst; he gives its m.p. as 120-122°.

20% sodium amalgam. 3 g of β-[1-methoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 177-179°, yielded 1 g of a lactone with a m.p. of 121-123° after recrystallization from alcohol to which charcoal had been added. The yield was 36% of the theoretical. The lactone of 1-[methoxy-(5,6,7,8)-tetrahydronaphthyl]-4-hydroxybutyric acid was a colorless, crystalline substance that was readily soluble in organic solvents but insoluble in water.

3.255 mg substance: 8.762 mg CO_2; 2.169 mg H_2O. Found %: C 73.41; H 7.45. $C_{15}H_{18}O_3$. Computed %: C 73.17; H 7.32.

b) Reduction of β-[1-methoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with Raney's alloy. 5 g of β-[1-methoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 177-179°, yielded 3 g of a substance with a m.p. of 122-124°. The yield was 64% of the theoretical. A test sample of this lactone, mixed with the lactone produced by sodium-amalgam reduction (m.p. 121-123°), fused at 122-124°.

3. The Lactone of [1-Propoxy-(5,6,7,8)-tetrahydronaphthyl-4]hydroxybutyric Acid.

Reduction of β-[1-propoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with 20% sodium amalgam. 9 g of β-[1-propoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid (m.p. 134-137°) yielded 3.4 g of colorless crystals with a m.p. of 81-83° after recrystallization from alcohol to which charcoal had been added; they were readily soluble in organic solvents and insoluble in water. The yield was 40% of the theoretical.

3.292 mg substance: 8.980 mg CO_2; 2.390 mg H_2O. 3.745 mg substance: 10.218 mg CO_2: 2.730 mg H_2O. Found %: C 74.39; 74.41; H 8.12, 8.16. $C_{17}H_{22}O_3$. Computed %: C 74.45; H 8.39.

4. The Lactone of [1-Butoxy-(5,6,7,8)-tetrahydronaphthyl-4]-hydroxybutyric Acid

a) Reduction of β-[1-butoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with 20% sodium amalgam. 2.5 g of β-[1-butoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 114-117°, yielded 0.7 g of colorless crystals with a m.p. of 83-87° after recrystallization from alcohol to which charcoal had been added. The yield was 30% of the theoretical.

2.696 mg substance: 7.395 mg CO_2; 2.012 mg H_2O. 3.010 mg substance: 8.250 mg CO_2; 2.220 mg H_2O. Found %: C 74.84, 74.75; H 8.35, 8.25. $C_{18}H_{24}O_3$. Computed %: C 75.00; H 8.33.

b) Reduction of β-[1-butoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with Raney's alloy. 2 g of β-[1-butoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 114-117°, yielded 1.6 g of the impure lactone. Recrystallization from alcohol and charcoal yielded 0.8 g of a substance with a m.p. of 84-87°. The yield was 42% of the theoretical. A test sample of this lactone, mixed with the lactone previously synthesized by sodium-amalgam reduction (m.p. 83-87°), fused at 84-87°.

5. The Lactone of [1-Hexoxy-(5,6,7,8)-tetrahydronaphthyl-4]-hydroxybutyric Acid

a) Reduction of β-[1-hexoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with 20% sodium amalgam. 17 ml of 10% Na_2CO_3 and 3 ml of alcohol were added to 0.9 g of β-[1-hexoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 92-94°, and then 14 g of 20% sodium amalgam was added gradually, with constant mechanical stirring. The usual treatment, followed by recrystallization from alcohol, yielded a substance with a m.p. of 65-75°. Triple recrystallization from alcohol yielded a crystalline substance with a m.p. of 81-82.5°, which was readily soluble in organic solvents, but insoluble in water.

3.618 mg substance: 10.035 mg CO_2; 2.829 mg H_2O. Found %: C 75.64; H 8.75. $C_{20}H_{28}O_3$. Computed %: C 75.96; H 8.86.

b) Reduction of β-[1-hexoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with Raney's alloy. 0.7 g of β-[1-hexoxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 92-94° yielded 0.2 g of a substance. Colorless crystals with a m.p. of 81-83° after recrystallization from alcohol to which charcoal had been added.

3.501 mg substance: 9.743 mg CO_2; 2.830 mg H_2O. Found %: C 75.90: H 9.04. $C_{20}H_{28}O_3$. Computed %: C 75.96; H 8.86.

6. The Lactone of [1-Heptyloxy-(5,6,7,8)-tetrahydronaphthyl-4]-hydroxybutyric Acid

Reduction of β-[1-heptyloxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid with 20% sodium amalgam. 20 ml of 10% Na_2CO_3 and 3 ml of alcohol were added to 1 g of β-[1-heptyloxy-(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 90-92°, and then 15 g of 20% sodium amalgam was added gradually, with mechanical stirring. The m.p. was 84-88° after the usual treatment and recrystallization from alcohol. The substance resembled the initial substance in its solubility in alcohol. In all probability this substance is a mixture of the lactone with the original substance. Many days of standing resulted in the separation of crystals from the mother liquor, which fused at 71-72° after triple recrystallization from alcohol. Elementary analysis of this substance proved that it was the lactone of (1-heptyloxytetrahydronaphthyl-4)-hydroxybutyric acid.

3.773 mg substance: 10.526 mg CO_2; 3.047 mg H_2O. Found %: C 76.09; H 9.04. $C_{21}H_{30}O_3$. Computed %: C 76.36; H 9.10.

7. The Lactone of [1-Hydroxy-(5,6,7,8)-tetrahydronaphthyl-4]-hydroxybutyric Acid

Reduction of β-[1-hydroxy-(5 6,7,8)-tetrahydronaphthoyl-4]-propionic acid with 20% sodium amalgam. 35 g of 20% sodium amalgam was added to 3 g of β-[1-hydroxy--(5,6,7,8)-tetrahydronaphthoyl-4]-propionic acid, with a m.p. of 192-194°, dissolved in 100 ml of 10% Na_2CO_3. After the usual treatment, the alkaline solution was acidulated with hydrochloric acid. The reaction product was not heated, as was done in all the other experiments. An ether extract was made, which was washed with 3% sodium bicarbonate and with water and then desiccated with sodium sulfate. After the ether had been driven off to small volume, the precipitate was filtered out and washed repeatedly with small batches of ether. Recrystallization from alcohol and charcoal yielded 0.8 g of a colorless crystalline substance with a m.p. of 152-153.5°.

4.197 mg substance: 11.153 mg CO_2; 2.705 mg H_2O. Found %: C 72.49; H 7.21. $C_{14}H_{16}O_3$. Computed %: C 72.42; H 6.90.

8. The Lactone of (2-Ethoxynaphthyl-6)-hydroxybutyric Acid

Reduction of (2-ethoxynaphthoyl-6)-propionic acid with Raney's alloy. 3 g of (2-ethoxynaphthoyl-6)-propionic acid, with a m.p. of 164-165°, yielded, after the usual treatment and recrystallization from alcohol, a crystalline substance with a m.p. of 125-126°. A.Danilova synthesized this lactone by reducing (2-ethoxynaphthoyl-6)-propionic acid with sodium amalgam; she gives its melting point as 125-126°.

9. The Lactone of (2-Propoxynaphthyl-6)-hydroxybutyric Acid

Reduction of (2-propoxynaphthoyl-6)-propionic acid with Raney's alloy. 5 g of (2-propoxynaphthoyl-6)-propionic acid yielded 1.2 g of a substance with a m.p. of 128-129° after recrystallization from alcohol to which charcoal had been added. A test sample of this lactone, mixed with the lactone previously synthesized by reduction with sodium amalgam (m.p. 127.5-129°), fused at 128-129°.

10. p-Methoxyphenyl-γ-butyrolactone

Reduction of p-methoxybenzoylpropionic acid with Raney's alloy. Reduction of

10 g of p-methoxybenzoylpropionic acid yielded 5 g of the substance. Colorless crystals with a m.p. of 52-54° after triple recrystallization from petroleum ether.

Rosenmund and Schapiro synthesized this lactone, with a m.p. of 53-55°, by reducing p-methoxybenzoylpropionic acid with palladium.

SUMMARY

1. It has been established that when β-(alkoxy aroyl)-propionic acids are reduced with Raney's alloy, the carbonyl group is reduced to a secondary alcohol group and γ-(alkoxy aryl)-hydroxybutyric acids are formed.

2. New γ-1-alkoxy-(hydroxy)-(tetrahydronaphthyl-4)-butyrolactones have been synthesized.

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DETERMINATION OF INTRAMOLECULAR HYDROGEN BONDS

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The ability of several organic compounds to form internal complex salts with metals – the lakes – has been known for a long time and has been investigated thoroughly [1].

Lakes are formed principally by:

a) Aromatic compounds in which some electronophilic group or atom (carbonyl, nitroso, azo, or tertiary heterocyclic nitrogen) is in the ortho or peri position to a hydroxyl (or less often, an amino) group;

b) Aliphatic compounds in which these groups are in the 1,3-position: 1,3-di ketones (acetylacetone) or 1,3-isonitroso ketones (isonitrosoacetylacetone).

It should be particularly noted that no lakes are formed when the reacting groups are in some other than the ortho or peri position. The formation of coordination compounds is accompanied, as a rule, by a deepening of the color and a sharp drop in solubility. Peri-hydroxycarbonyl compounds (alizarin [2]), derivatives of o-hydroxycarboxylic acids (chrome and mordant azo dyes containing a carboxyl group [3]), nitroso dyes [4], o-hydroxy azo dyes [5], 8-hydroxyquinoline [6], 1,3-diketones (acetylacetone [7], 1,3-nitrosoamines (nitrosoguanidine [8]), and nitroso-oximes (dimethylglyoxime [1]) – all of these diverse groups of organic compounds form insoluble complex inner salts, which are often intensely colored, with many of the metals (B, Ba, Ca, Al, Fe, Cr, Co, Pt, and others) (cf Table 1, upper row).

TABLE 1

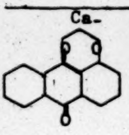
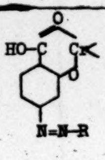
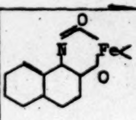
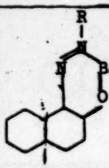
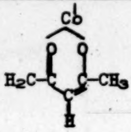
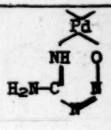
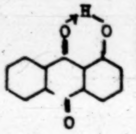
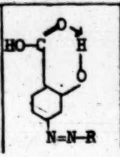
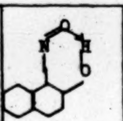
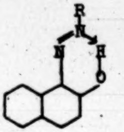
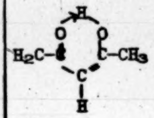
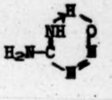
					

TABLE 1 (Continued)

Boron acetate, extensively investigated by Dimroth [9], has proved to be a particularly suitable substance, capable of forming extremely stable complex inner salts that are highly colored and often possess strong fluoresence. Dimroth chiefly studied the nature of the products formed by the reaction of boron acetate with hydroxy and aminoanthraquinones. But it turned out that this reaction applied to many compounds of the benzene, naphthalene, and anthraquinone series, which contained the above-mentioned electronophilic groups in the ortho or peri position to the OH or NH_2 groups. No lakes were formed when the positions of the OH or NH_2 groups were different; we secured slightly colored, slightly acylated molecular compounds with boron acetate (cf Tables 2 and 3, upper rows). Hence, it may be considered proved beyond doubt that metals which form such intramolecular coordination compounds replace the hydrogen in a hydroxyl (or, less frequently, an amino) group, forming a chemical bond with it, and react, via their extra valencies, with the electronophilic groups. These coordination compounds must constitute six- or five-membered rings. In all the instances listed above, the organic molecules that form inner coordination compounds can also form hydrogen bonds (cf the bottom rows in Tables 1, 2, and 3). There are individual references to this in the literature.

TABLE 2

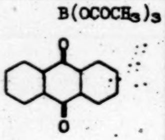
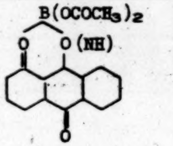
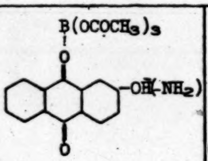
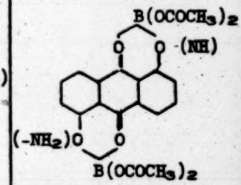
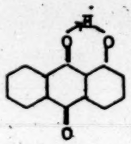
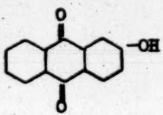
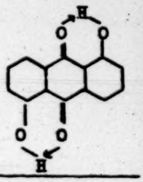
			
Slightly colored, unstable	Intensely colored, cannot be acylated	Slightly colored, can be acylated	Intensely colored cannot be acylated
-			
-	Hydrogen bond is formed	No hydrogen bond is formed	Hydrogen bond is formed

TABLE 3

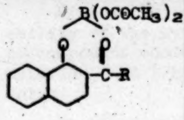
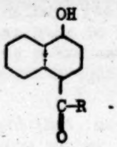
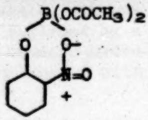
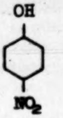
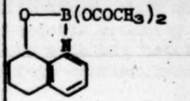
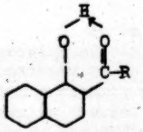
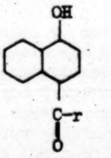
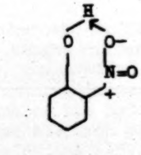
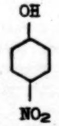
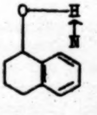
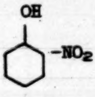
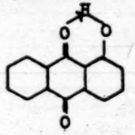
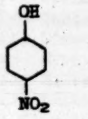
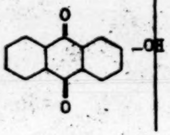
				
Intensely colored, cannot be acylated	No coloring with $B(OCOCH_3)_3$, can be acylated	Intensely colored, not recovered	No coloring with $B(OCOCH_3)_3$	Cannot be acylated
				
Hydrogen bond is formed	No hydrogen bond is formed	Hydrogen bond is formed	No hydrogen bond is formed	Hydrogen bond is formed

TABLE 4

Formula	Dissociation constant	Formula	Dissociation constant
	6.8×10^{-8}		6.2×10^{-12}
	$.7 \times 10^{-8}$		7×10^{-8}

Errera [10] and Hilbert [11] state, without making any generalizations, that the ability of the hydrogen atom to be replaced by a metal is a characteristic property of compounds containing a hydrogen bond; 2-hydroxyacetophenone reacts with tin tetrachloride, and 1-hydroxyanthraquinone reacts with boron acetate, to form complex inner salts.

It shoudl be noted that, according to modern concepts of the hydrogen bond [12] its existence in a large number of compounds has been demonstrated with convincing evidence by means of infrared spectroscopy [12,13] and by arguments of a physicochemical nature [14] and, in certain instances, of a chemical nature [15,16]. It may be assumed that the formation of a lake is in many instances a qualitative reaction for the presence of a hydrogen bond. The numerous examples cited indicate that the ability of compounds to form lakes is in full agreement with the existence of a hydrogen bond within them, which is the cause of the lake formation.

It is essential to note that the difficulty involved in producing the boron acetates of o-nitrophenols and the slight difference between the dissociation constants of o- and p-nitrophenols, compared to the difference between the dissociation constants of 1- and 2-hydroxyanthraquinones (cf. Table 4), and - as the apparent results thereof - the lower strength of the hydrogen bond in o-nitrophenol, may be due to the fact that the shift of an electron pair from the hydroxyl to the nitro group, which increases the mobility of the hydrogen atom, masks the stabilizing effect of the hydrogen bond.

SUMMARY

The ability of aromatic hydroxy (and, less frequently, amino) compounds that contain some electronophilic group (carbonyl, azo, etc.) in the ortho or peri position, and of aliphatic compounds that contain these groups in the 1,3 position, to form lakes when reacted with metals proves that in their free state these compounds possess a hydrogen bond.

It may therefore be supposed that lake formation of this sort may serve as a qualitative reaction for a hydrogen bond. The converse conclusion cannot be stated; not every compound possessing a hydrogen bond can form lakes (complex inner salts).

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[15] Ufimtsev, J.Gen.Chem. 13, 520 (1943).

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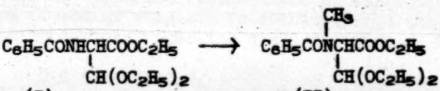
THE METHYLATION OF THE DIETHYL ACETAL OF FORMYL HIPPURATE

A Ya Berlin, V I Maimind and E. S. Golombik

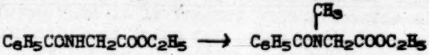
In our study of the chemistry of penicillin-like substances and of the products of their degradation, we undertook an investigation of compounds of the type of penaldinic acid, $RCONHCH(CHO)COOR'$. In the present research, in particular, we set as our goal a study of the feasibility of synthesizing the diethyl acetal of N-methylformyl hippurate (II) from the diethyl acetal of formylhippuric acid (I):



$$C_6H_5CONH\underset{CH(OC_2H_5)_2}{CH}COOC_2H_5 \longrightarrow C_6H_5CO\overset{CH_3}{N}\underset{CH(OC_2H_5)_2}{CH}COOC_2H_5$$

(I) (II)

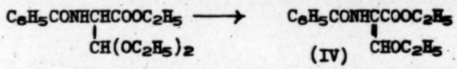
Comparatively little has been done on the alkylation of acid amides. The alkyl amides are most often synthesized by alkylating the corresponding alkyl amines. In this connection we methylated an ester of hippuric acid, a substance that is much more accessible than the diethyl acetal of formylhippuric acid, by way of a preliminary experiment:



$$C_6H_5CONHCH_2COOC_2H_5 \longrightarrow C_6H_5CO\overset{CH_3}{N}CH_2COOC_2H_5$$

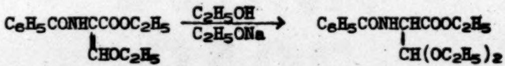
(III)

There is no description in the literature of a method for the synthesis of the ethyl ester of benzoylsarcosine (III); the benzoylsarcosine itself is produced in the usual manner - by benzoylating sarcosine [1]. There are no specifications for the synthesis of benzoylsarcosine by the methylation of hippuric acid. The methylation of the hippurate is relatively simple - the sodium derivation of the hippurate, prepared by reacting metallic sodium with a solution of the hippurate in absolute xylene at 110-120°, is treated with dimethyl sulfate. The reaction results in the production of the ethyl ester of benzoylsarcosine, benzoylsarcosine (with a m.p. of 100-101°) being produced from the latter by saponification. On the other hand, the methylation of the diethyl acetal of formyl hippurate, which we effected by analogy with the synthesis of the ester of benzoylsarcosine, proved to be fairly complicated. In our first experiments on the methylation of the diethyl acetal of formyl hippurate under the same conditions, the reaction was extremely violent, and the reaction solution evolved considerable tar. The reaction resulted in the recovery of a negligible quantity of an oily substance, saponification of which with an alcoholic alkali yielded a crystalline acid with a m.p. of 211-212°, which did not contain a methylimide group. The structure of this compound was determined subsequently. Inasmuch as the reaction was very violent, and we were unable to secure a methylation product attached to the nitrogen, we carried out our subsequent experiments under milder conditions and in an atmosphere of nitrogen. During the first stage of the reaction (preparation of the sodium derivative) in absolute benzene at 50-60°, only little hydrogen was evolved; the metallic sodium was covered with a film, and the reaction soon came to an end. The reaction product, secured by treatment with dimethyl sulfate, followed by a refining process, was a crystalline substance with a m.p. of 117°. Analysis indicated that its composition corresponded to the formula $C_{14}H_{17}O_4N$. This substance does not contain a methylimide group. The foregoing data identify the substance with a m.p. of 117° as the product of the cleavage of 1 molecule of alcohol from the diethyl acetal of formyl hippurate. The absence of a methylimide group leads one to suppose that the substance with a m.p. of 117° is formed during the first stage of the reaction. In fact, the same substance was secured when the diethyl acetal of formyl hippurate was reacted with a suspension of metallic sodium in absolute benzene, with no dimethyl sulfate present. Moreover, it was found that thionyl chloride has the same effect as metallic sodium, and that when the former was used, the same compound with a m.p. of 117° was recovered from the initial diethyl acetal of formyl hippurate. The properties of the synthesized substance indicate beyond a doubt that it is ethoxymethylene hippurate (IV):



$$C_6H_5CONH\underset{\substack{|\\ CH(OC_2H_5)_2}}{C}HCOOC_2H_5 \longrightarrow \underset{(IV)}{} C_6H_5CONH\underset{\substack{\|\\ CHOC_2H_5}}{C}COOC_2H_5$$

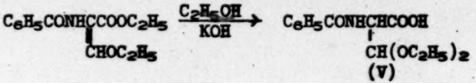
Ethoxymethylene hippurate readily adds elements of alcohol: when it is reacted with a solution of sodium ethylate in absolute ethyl alcohol at room temperature it is converted, with good yield, into the diethyl acetal of formyl hippurate:



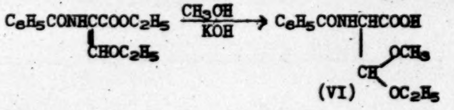
$$C_6H_5CONH\underset{\substack{\|\\ CHOC_2H_5}}{C}COOC_2H_5 \xrightarrow[C_2H_5ONa]{C_2H_5OH} C_6H_5CONH\underset{\substack{|\\ CH(OC_2H_5)_2}}{C}HCOOC_2H_5$$

To identify this compound, it was converted into the corresponding amide by the action of alcoholic ammonia.

The addition of alcohol elements to ethoxymethylene hippurate takes place so readily as to occur even when it is treated with alcoholic alkali; when this is done, not only is the ethoxymethylene group not hydrolyzed, but, on the contrary, an acetal of formylhippuric acid is formed, in addition to the saponification of the carbethoxy group. In fact, when the ester was saponified with a solution of KOH in C_2H_5OH, we obtained a crystalline substance that proved to be the diethyl acetal of formylhippuric acid (V). Even when a large excess of the alkali was used, the consumption of the latter did not exceed one mol. Substituting methanol for ethyl alcohol in this reaction results in the formation of the mixed ethyl methyl acetal of formylhippuric acid (VI):

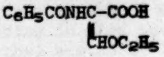


$$C_6H_5CONH\underset{\substack{\|\\ CHOC_2H_5}}{C}COOC_2H_5 \xrightarrow[KOH]{C_2H_5OH} C_6H_5CONH\underset{\substack{|\\ CH(OC_2H_5)_2\\ (V)}}{C}HCOOH$$



$$C_6H_5CONH\underset{\substack{\|\\ CHOC_2H_5}}{C}COOC_2H_5 \xrightarrow[KOH]{CH_3OH} C_6H_5CONH\underset{\substack{|\\ CH(OCH_3)(OC_2H_5)\\ (VI)}}{C}HCOOH$$

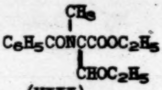
It might have been thought that the first thing happening in this reaction was the addition of the alcohol elements, as a result of which the formation of the acetal group proves to be unaffected by the action of the alkali. It was found, however, that even when the KOH was dissolved in dioxane, only 1 mol of the alkali was again consumed, while the reaction resulted in the formation of a substance that did not contain a free hydroxymethyl group and proved to be ethoxymethylenehippuric acid (VII). When alcoholic ammonia was reacted with the ethoxymethylenehippuric ester, only one carbethoxy group again entered into the reaction, and the amide of ethoxymethylenehippuric acid was formed. Thus, the ethoxymethylene group in the ethoxymethylenehippuric ester proves to be highly resistant to the action of alkalies, in this respect differing greatly from the ethoxymethylene derivatives of the maleates and the acetoacetates: acetyl-acetone [2] and 2-phenyl-4-ethoxymethylene-oxazolinone-5, which are converted with extraordinary ease into the corresponding hydroxymethylene compounds when acted upon by alkalies and sometimes even when shaken up with water; the carbethoxy group in the esters remains unchanged.



$$\begin{array}{l} C_6H_5CONHC\text{-}COOH \\ \qquad\qquad\ \ \| \\ \qquad\qquad\ \ CHOC_2H_5 \end{array}$$

(VII)

As has been pointed out above, the formation of ethoxymethylene hippurate in the course of our endeavors to methylate the diethyl acetal of formyl hippurate was always accompanied by the formation of a film that covered the metallic sodium and prevented the formation of the sodium derivative of the diethyl acetal of formyl hippurate. We therefore ran the succeeding tests with carefully purified (cryoscopic) absolute benzene. It was found that the reaction follows a different course under these conditions and that all the sodium reacts. Methylation in an atmosphere of nitrogen at 50-60° resulted in the preparation of an oily substance, which distilled in vacuum at 148-156° (0.3 mm) and crystallized upon cooling. Careful analysis of the reaction product indicated that it consists of two substances, the physical properties of which were very much alike. One of them, with a m.p. of 72.5°, proved to be the principal reaction product, the other product, only a slight quantity of which was produced, having a m.p. of 70.5°. A mixed test sample of these two products exhibited a sharp depression of the melting point. A series of test run under varying conditions indicated that the substance with a m.p. of 70.5° might be the principal reaction product if the reaction were carried out at 100-110° (in absolute xylene); under these conditions the substance with a m.p. of 72.5° is either not formed at all or is formed in a negligibly minute quantity. The analysis data and the properties of the substance with a m.p. of 72.5° showed that it is an ester of ethoxymethylenebenzoylsarcosine (VIII). The behavior of this substance toward alkalies reminds one of the ester of ethoxymethylenehippuric acid described above. Thus, when reacted with alcoholic KOH under various conditions for saponification, only 1 mol of KOH is consumed, no matter how much of the alkali is taken; only the carbethoxy group is saponified, inasmuch as the reaction product does not contain a free hydroxymethylene group. Similarly, the action of an alcoholic solution of ammonia results in the formation of an amide of ethoxymethylene-N-methylhippuric acid, with a m.p. of 203-214.5°, which is not changed when it is treated with an alcoholic alkali. On the other hand, the ester of ethoxymethylenebenzoylsarcosine differs sharply from the ethoxymethylene hippurate in its ability to add alcohol elements. This compound cannot be converted into the corresponding acetal by means of absolute C_2H_5OH, when either various catalysts (C_2H_5ONa, HCl, $ZnCl_2$) are used or the temperature and other reaction conditions are changed.

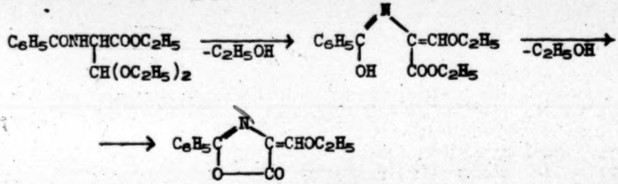


$$\begin{array}{l} \qquad\quad CH_3 \\ \qquad\quad\ | \\ C_6H_5CONCCOOC_2H_5 \\ \qquad\qquad\ \| \\ \qquad\qquad CHOC_2H_5 \end{array}$$

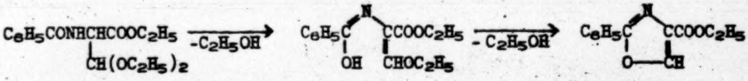
(VIII)

Analysis of the other substance (with a m.p. of 70.5°) recovered in the methylation of the diethyl acetal of formyl hippurate showed that it does not contain a methylimide group, while its composition ($C_{12}H_{11}O_3N$) indicated it to be the product of the cleavage of two molecules of ethyl alcohol from the original acetal ester. This substance is, in fact, also produced when a xylene solution of the diethyl acetal of formyl hippurate is heated with metallic sodium to 100-110°, even without subsequent treatment of the reaction mixture with dimethyl sulfate. In view of this and bearing in mind the fact that ethoxymethylene hippurate is readily produced from the diethyl acetal of formyl hippurate by the action of metallic sodium, we may conceive of the reaction involving the formation of the substance with a m.p. of 70.5° as following one of the two following patterns:

1)

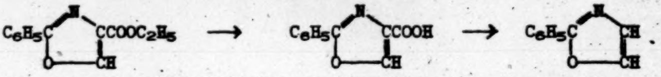


2)



(IX)

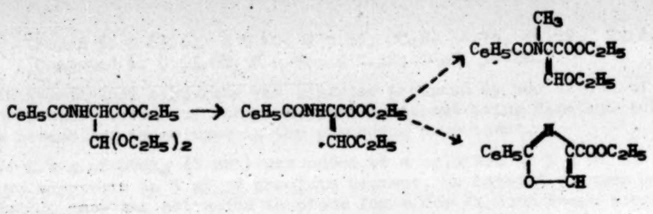
The first of these equations is excluded if for no other reason than that the end product of the reaction would then have had to be our 2-phenyl-4-ethoxymethylene-oxazolinone-5, which fuses at 99-100°. Hence, the only other possible assumption is that the synthesized substance with a m.p. of 70.5° is the ethyl ester of 2-phenyloxazole-4-carboxylic acid (IX). This assumption proved to be correct, and the structure of this reaction product was proved by saponifying it to 2-phenyloxazole-4-carboxylic acid (X) (m.p. 211-212°) and decarboxylating the latter to 2-phenyloxazole (XI), which was identified as its picrate [3]:



(X) (XI)

As has been pointed out above, in our initial endeavors to methylate the diethyl acetal of formyl hippurate under severe conditions we secured an oily substance that yielded an acid with a m.p. of 211-212° upon saponification; the latter proved to be identical with 2-phenyloxazole-4-carboxylic acid (X).

The foregoing suggested that the ethoxymethylene hippurate is an intermediate product in the reaction under discussion, formed by the action of metallic sodium upon the diethyl acetal of formyl hippurate. Experiments we ran actually showed that the same substance is secured from ethoxymethylene hippurate as from the diethyl acetal of formyl hippurate. Thus, when the reaction is carried out in absolute benzene at 50-60°, we get principally ethoxymethylene-N-methyl hippurate, whereas at 110-120° in absolute xylene nothing but the ester of 2-phenyloxazole-4-carboxylic acid is formed. Thus, the mechanism of the reaction involving the methylation of the diethyl acetal of formyl hippurate may be represented as follows:



EXPERIMENTAL*

1. Ethyl Ester of Benzoylsarcosine (III)

0.72 g of metallic sodium and 50 ml of absolute xylene were placed in a three-necked flask, fitted with a thermometer and a dropping funnel. A solution of 6.5 g of the hippuric ester in 100 ml of absolute xylene was added, with constant stirring while a current of nitrogen was passed through the mixture, to the suspension of sodium in absolute xylene heated to 100-110°. Hydrogen was evolved vigorously, and a white precipitate of the sodium derivative of the hippuric ester settled out. After all the metallic sodium had disappeared, the reaction mixture was heated for 2 hours to 100-110°. Then 4 g of dimethyl sulfate was added gradually, with chilling and vigorous stirring. The reaction solution was then heated for an hour to 100°. When the reaction was over, the solution was poured into ice water, and the xylene layer was separated, washed with water, and desiccated with calcined sodium sulfate. Driving off the xylene in vacuum yielded 3.8 g of an oily substance that distilled as a thick, nearly colorless liquid at 152-156° (2 mm), 138-139° (0.4 mm), and 141° (0.6 mm), and crystallized upon cooling. M.p. 33-34.5°. The yield was 54% of the theoretical.

3.024 mg substance: 7.189 mg CO_2; 1.788 mg H_2O. Found %: C 64.83; H 6.61. $C_{12}H_{15}O_3N$. Computed %: C 65.16; H 6.79.

Saponification with an alcoholic alkali yielded benzoylsarcosine, with a m.p. of 100-101°, which agrees with the figure given in the literature [1]:

Found %: NCH_3 14.80. Equiv. 193.3. $C_{10}H_{11}O_3N$. Computed %: NCH_3 15.03. Equiv. 193.

2. Ethoxymethylene Hippurate (IV)

a) A solution of 4.4 g of the diethyl acetal of formyl hippurate in 40 ml of absolute benzene was added, with stirring, to a suspension of 0.45 g of sodium in 125 ml of absolute benzene heated to 60°; hydrogen was seen to evolve. After 10-15 minutes had elapsed the sodium was covered with a dark film, and the evolution of hydrogen ceased. The reaction solution was heated for 2 more hours to 60°; after it had cooled, a solution of 5 g of dimethyl sulfate in 10-15 ml of absolute benzene was added with vigorous stirring. After the dimethyl sulfate had been added, the reaction solution was heated to 50-60°, for 1 hour. Upon cooling, the solution was decanted from the unreacted metallic sodium and poured into ice water. The benzene layer was separated and washed with water, a 5% solution of K_2CO_3, and water, and then desiccated with calcined sodium sulfate. The residue left after the solvent had been driven off was distilled. This yielded a thick, colorless liquid with a b.p. of 168-170° (at 0.35 mm), which crystallized from petroleum ether when rubbed. Suction filtering yielded 1.9 g of a substance with a m.p. of 109°, which crystallized from benzene to which petroleum ether had been added as colorless platelets with a m.p. of 116.5-117°, which are readily soluble in most organic solvents, but insoluble in petroleum ether.

3.623 mg substance: 8.451 mg CO_2; 2.079 mg H_2O. 4.987 mg substance: 0.230 ml N_2 (19°, 738 mm). 7.105 mg substance: 16.47 ml 0.01 N H_2SO_4. 7.083 mg. substance: 16.3 ml. 0.01 N H_2SO_4.

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* With the assistance of E. G. Gusakova and V. P. Katanova.

Found %: C 63.61 H 6.42; N 5.23; OC_2H_5 34.73, 34.52. $C_{14}H_{17}O_4N$.
Computed %: C 63.88; H 6.46; N 5.32; OC_2H_5 34.22.

Ethoxymethylene hippurate was likewise produced by the action of metallic sodium upon the diethyl acetal of formyl hippurate without using dimethyl sulfate, under conditions resembling those used in the preceding experiment.

b) 0.4 g of $SOCl_2$ (1 mol) was added to a solution of 1 g of the diethyl acetal of formyl hippurate in 5 ml of absolute benzene; no outward changes were observed. The reaction mass was set aside to stand for a day at room temperature. The next day the solvent was driven off, and the residue distilled in vacuum. This yielded 0.6 g of a substance that distilled at 168-173° at 0.3 mm as a thick, colorless liquid, which crystallized upon cooling. The melting point of this substance was 116°; a test sample, mixed with the substance obtained in the preceding experiment, exhibited no depression of the melting point.

Amide of ethoxymethylenehippuric acid. 15 ml of a 12% alcoholic solution of ammonia was added to 1 g of ethoxymethylene hippurate. The next day the solvent was driven off in vacuum, and the residue was recrystallized from benzene. This yielded colorless prisms with a m.p. of 116.5°, which were readily soluble in alcohol and acetone, less so in benzene, chloroform, and carbon tetrachloride, and insoluble in cold water. A test sample mixed with the initial ester exhibited considerable depression. The substance can also be recrystallized from water.

4.913 mg substance: 4.28 ml 0.01N H_2SO_4. 7.630 mg substance: 6.67 ml 0.01N H_2SO_4. Found %: N 12.20, 12.24. $C_{12}H_{14}O_3N_2$. Computed %: N 11.97.

3. Diethyl Acetal of Formyl Hippurate from Ethoxymethylene Hippurate (IV ⟶ I)

2 g of ethoxymethylene hippurate was added to a solution of 0.15 g of C_2H_5ONa in 30 ml of absolute C_2H_5OH. The resulting solution was allowed to stand for 1 hour at room temperature, after which it was heated for 1 hour to 50°. The next day the solvent was driven off, the residue was poured into ice water, and the mixture was neutralized with acetic acid. The resulting oil was extracted with ether, and the ether solution was washed with water and a solution of bicarbonate and then desiccated with calcined Na_2SO_4. After the solvent had been driven off, the residue consisted of a thick, colorless liquid, which crystallized when kept in a vacuum exsiccator. Recrystallization from petroleum ether (b.p. 43-52°) yielded colorless prisms with a m.p. of 48-49.5°, which proved to be identical with the diethyl acetal of formyl hippurate.

The diethyl acetal of formylhippuramide was secured by treating the resulting ester with an alcoholic solution of ammonia. Colorless prisms with a m.p. of 172.5° (from water), soluble in most organic solvents, with the exception of ether and petroleum ether.

5.495 mg substance: 4.03 ml 0.01N H_2SO_4. 6.536 mg substance: 13.83 ml 0.02N $Na_2S_2O_3$. Found %: N 10.27; OC_2H_5 31.76. $C_{14}H_{20}O_4N_2$. Computed %: N 10.0; OC_2H_5 32.14.

4. Saponification of Ethoxymethylene Hippurate

a) Action of a solution of KOH in ethyl alcohol. 0.1463 g of ethoxymethylene hippurate was dissolved in 5 ml of an approximately 0.5 N KOH solution in ethyl alcohol (25.95 ml of 0.1 N HCl was required to neutralize 5 ml of this alkali solution). The next day the excess alkali was neutralized with 0.1N HCl; 20.15 ml of 0.1N HCl was consumed. Hence, the KOH consumed in saponifying the ethoxymethylene hippurate corresponded to approximately 1.08 mol. The neutral solution was evaporated in vacuum to a volume of 1 ml and treated, with chilling, with hydrochloric acid (1:3) until its reaction to Congo was acid. The resulting oil was extracted with ether, washed with water, and desiccated with calcined Na_2SO_4. After the solvent had been driven off, the crystalline residue was recrystallized from benzene to which petroleum ether had been added. This yielded colorless needles with a m.p. of 91-92° (with decomposition), which are readily soluble in 5% NaOH, in a solution of $NaHCO_3$, and in most organic solvents. The substance does not exhibit the coloring with $FeCl_3$ that is characteristic of a hydroxymethylene group.

A test sample of this substance, mixed with the diethyl acetal of formylhippuric acid (V), exhibited no depression of the melting point.

3.050 mg substance: 6.666 mg CO_2; 3.050 mg H_2O. Found %: C 59.61; H 6.87. $C_{14}H_{19}O_5N$. Computed %: C 59.79; H 6.77.

b) Action of a solution of KOH in methanol. 1.0 g of ethoxymethylene hippurate was dissolved in 35 ml of an approximately 0.5 N solution of KOH in CH_3OH (23.1 ml of 0.1 N HCl was required to neutralize 5 ml of this alkali solution). The next day the excess KOH was neutralized with 12.2 ml of 0.1N HCl; hence, 1.04 mols of KOH were consumed. Then the reaction solution was given the same treatment as in the preceding experiment. This yielded 0.8 g of the ethyl methyl acetal of formylhippuric acid (VI) as colorless needles with a m.p. of 88-89° with decomposition (from benzene), which are readily soluble in 5% NaOH and in a bicarbonate solution and are not colored by $FeCl_3$. A test sample, mixed with the diethyl acetal of formylhippuric acid (V), exhibited a depression of the melting point.

3.898 mg substance: 8.369 mg CO_2; 2.230 mg H_2O. 7.172 mg substance: 0.353 ml N_2 (22°, 733 mm). Found %: C 58.55; H 6.40; N 5.50. $C_{13}H_{17}O_5N$. Computed %: C 58.42; H 6.37; N 5.24.

c) Action of a solution of KOH in dioxane. 35 ml (4 mols) of an approximately 3% solution of KOH in 50% aqueous dioxane was added to 1 g (1 mol) of ethoxymethylene hippurate. The solution was treated as in the preceding experiments. This yielded 0.5 g of a substance in the form of colorless platelets with a m.p. of 188-189° (from water), which were soluble in 5% NaOH or a bicarbonate solution and exhibited no color when treated with $FeCl_3$.

A test sample, mixed with ethoxymethylene hippuric accid (VII) produced by a different method, exhibited no depression of the melting point.

5. Methylation of the Diethyl Acetal of Formyl Hippurate

A. Ethoxymethylene-N-methyl Hippurate (VIII)

A solution of 2 g of the diethyl acetal of formyl hippurate in 20 ml of absolute benzene* was added, with stirring, in an atmosphere of nitrogen to a suspension of 0.15 g of sodium (in powder form) in 60 ml of absolute benzene, heated to 50-60°; hydrogen was vigorously evolved, and a white precipitate was thrown down. After the reaction was complete, 1-1.5 hours later, the reaction mixture was heated for an hour to 50° and then treated with a solution of 1.6 g of dimethyl sulfate in 10 ml of absolute benzene. The solution was then heated to 50-60° for 1 hour and poured into ice water after it had cooled. The benzene layer was given the same treatment as in the methylation of the hippuric ester. The residue left after the benzene had been driven off was distilled in vacuum. This yielded 1.3 g of a nearly colorless oil, which distilled at 148-156° (at 0.3 mm) and crystallized upon cooling. Triple recrystallization from petroleum ether (b.p. 52-65°) yielded thin colorless needles with a m.p. of 71-72.5°, which were readily soluble in most organic solvents (except petroleum ether), and were insoluble in 5% HCl or 5% NaOH.

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*The benzene was purified by freezing out and by heating with aluminum chloride, followed by washing with water and with a soda solution, desiccated with $CaCl_2$, distillation and dehydration with metallic sodium.

3.267 mg substance: 7.798 mg CO_2; 1.988 mg H_2O. 9.448 mg substance: 3.35 ml 0.01 N H_2SO_4. 19.5 mg substance: 13.73 ml 0.05 N $Na_2S_2O_3$. 41.27 ml 0.05 N $Na_2S_2O_3$. Found %: C 65.10; H 6.81; N 4.96; NCH_3 6.82; OC_2H_5 31.77. M 277, 279 (according to Rast). $C_{15}H_{19}O_4N$. Computed %: C 64.98; H 6.86; N 5.05; NCH_3 10.5; OC_2H_5 32.5; M 277.

Evaporation of the mother liquors yielded a negligible quantity of colorless crystals with a m.p. of 67.5°, which were soluble in most organic solvents. Repeated recrystallizations from petroleum ether (b.p. 52-65°) yielded colorless needles with a m.p. of 70.5°. A test sample, mixed with ethoxymethylene-N-methyl hippurate, exhibited a marked depression of the melting point (the mixed test sample fused at 48°). Further details of this substance are given below.

a) Amide of ethoxymethylene-N-methylhippuric acid. Treating the ethoxymethylene-N-methyl hippurate with alcoholic ammonia yielded the amide of ethoxymethylene-N-methylhippuric acid. Double recrystallization from 50% aqueous CH_3OH yielded colorless needles with a m.p. of 203-204.5°, which were soluble in most organic solvents, but were insoluble in water, petroleum ether, 5% NaOH, and dilute HCl.

5.403 mg substance: 4.36 ml 0.01 N H_2SO_4. 5.882 mg substance: 4.76 ml 0.01 N H_2SO_4. 7.055 mg substance: 5.42 ml 0.05 N $Na_2S_2O_3$. 8.36 ml 0.05 N $Na_2S_2O_3$. Found %: N 11.31: 11.32. NCH_3 7.44; OC_2H_5 17.79. M 233 240 (according to Rast). $C_{13}H_{16}O_3N_2$. Computed %: N 11.29; NCH_3 11.69; OC_2H_5 18.15. M 248.

This amide is unaffected by treatment with an excess of 3% alcoholic NaOH at room temperature, as well as by boiling it for 6 hours with a 10% alcoholic solution of KOH. When it is treated with concentrated HCl at room temperature, benzoic acid begins to be liberated within 15-20 minutes.

b) Saponifying ethoxymethylene-N-methyl hippurate. 0.2664 g of ethoxymethylene-N-methylhippurate was dissolved in 9 ml of an approximately 0.5 N solution of KOH in C_2H_5OH (neutralization of 9 ml of this KOH solution required 8.62 ml of 0.5 N HCl). The next day the solution was neutralized with 6.54 ml of 0.5N HCl. Thus, 1.08 mols of KOH were required to saponify the ethoxymethylene-N-methyl hippurate. Suitable treatment (cf the experiments on the saponification of ethoxymethylene hippurate) yielded an oily substance that did not crystallize, either upon cooling or when kept for a long time in a vacuum exsiccator. This substance had an acid reaction, was soluble in alkalies, and did not exhibit the color reaction with $FeCl_3$ that is characteristic of a hydroxymethylene group. The same substance can be produced by boiling the original ester with 5% alcoholic KOH; in this case the KOH consumed for saponification totals 1 mol. Ethoxymethylene-N-methyl hippurate is unaffected by concentrated HCl at room temperature; heating it for 10-15 minutes over a water bath results in the abundant evolution of benzoic acid.

c) Experiments on adding alcohol elements to ethoxymethylene-N-methyl hippurate. 0.85 g of ethoxymethylene-N-methyl hippurate was added to a solution of 0.2 g of C_2H_5ONa in 15 ml of absolute C_2H_5OH. The solution was then heated to 60° for 6 hours. The oil recovered after the alcohol had been driven off and the residue had been neutralized with acetic acid was extracted with ether, washed with water, and desiccated with Na_2SO_4. The residue left after the ether was driven off was the original ethoxymethylene-N-methyl hippurate. The same results were obtained when the quantity of sodium ethylate was increased and the reaction mixture was boiled. 25 ml of a 4% solution of HCl in absolute ethyl alcohol was added to 0.5 g of ethoxymethylene-N-methyl hippurate. The solution was boiled for 4 hours. After the alcohol had been driven off, the residue was treated in the cold with a 5% solution of K_2CO_3 and then with ether. The ether solution was washed with water and desiccated with calcined Na_2SO_4. After the solvent was driven off, the residue was found to consist of the original ethoxymethylene-N-methyl hippurate plus a negligible quantity of ethyl benzoate. Saponification of the latter with alcoholic alkali yielded benzoic acid. 0.1 g of anhydrous $ZnCl_2$ was added to a solution of 0.5 g of ethoxymethylene-N-methyl hippurate in 15 ml of absolute C_2H_5OH. The next day the alcohol was driven off in vacuum and the residue was treated with water, which yielded the original substance.

B. Ethyl Ester of 2-Phenyloxazole-4-carboxylic Acid (IX)

A solution of 2 g of the diethyl acetal of formyl hippurate in 25 ml of absolute xylene was added, with stirring, in an atmosphere of nitrogen to a suspension of 0.15 g of Na in 60 ml of absolute xylene heated to 110-120°. The reaction was extremely violent, with considerable tarring. Treatment of the reaction solution with dimethyl sulfate and subsequent purification (cf the synthesis of ethoxymethylene-N-methyl hippurate above) yielded a minute quantity of an ester of phenyloxazolecarboxylic acid as a thick, colored liquid, which distilled at 146-153° (at 0.6 mm). Saponification with alcoholic alkali yielded the corresponding acid, with a m.p. of 211° (cf below). The best results were obtained when this experiment was run at 100-110°. This yielded 0.5 g of a substance that distilled at 140-145° (at 0.3 mm) as a thick, nearly colorless liquid that crystallized upon cooling. Recrystallization from petroleum ether yielded colorless crystals with a m.p. of 70.5°. The properties of the synthesized ester of phenyloxazolecarboxylic acid and the absence of any depression of the melting point in a mixed test sample proved that the ester was identical with the substance with the same melting point that had been produced by methylating the diethyl acetal of formyl hippurate at 50-60° (*vide supra*).

> 3.889 mg substance: 9.418 mg CO_2; 1.840 mg H_2O. 8.220 mg substance: 0.500 ml N_2 (27°, 739.6 mm). Found %: C 66.05; H 5.29; N 6.76. $C_{12}H_{11}O_3N$. Computed %: C 66.36; H 5.07; N 6.45.

The same substance was synthesized by treating the diethyl acetal of formyl hippurate with metallic sodium at 100-110°, without using dimethyl sulfate.

6. Methylation of Ethoxymethylenehippuric Ester

a) The experiment was carried out at 50-60° in absolute benzene, thus resembling the methylation of the diethyl acetal of formyl hippurate. The reaction resulted in the recovery of a substance with a m.p. of 72°, which was identical with the ethoxymethylene-N-methyl hippurate. In a parallel test, a small quantity of the ester of 2-phenyl-oxazole-4-carboxylic acid, with a m.p. of 70.5°, was secured, in addition to the ethoxymethylene-N-methyl hippurate.

b) A similar experiment was run at 100-110° in absolute xylene. Suitable treatment resulted in the recovery of 0.9 g (from 3.7 g of the ethoxymethylenehippuric ester) of a crystalline substance, which had a m.p. of 70.5° after recrystallization from petroleum ether and exhibited no depression when mixed in a test sample with the previously prepared ester of 2-phenyloxazole-4-carboxylic acid. The same ester of 2-phenyloxazole-4-carboxylic acid was synthesized by treating ethoxymethylenehippuric ester with metallic sodium at 100-110°, without using dimethyl sulfate.

7. 2-Phenyloxazole-4-carboxylic Acid (X)

0.25 ml of NaOH (~40%) was added to a solution of 0.2 g of the ester of 2-phenyloxazole-4-carboxylic acid in 3 ml of C_2H_5OH. The reaction mixture crystallized within a few minutes. The next day the mixture was dissolved in 5 ml of ice water and treated with hydrochloric acid (1:3) until it exhibited an acid reaction to Congo. After recrystallization from 25% aqueous C_2H_5OH the resulting crystals (0.15 g) consisted of thin colorless needles with a m.p. of 212-212.5°, which were readily soluble in 5% NaOH and in a solution of $NaHCO_3$. A test sample, mixed with the substance synthesized by saponifying the product of the methylation of the diethyl acetal of formyl hippurate at 100-120° (vide supra), exhibited no depression of the melting point.

3.213 mg substance: 7.509 mg CO_2; 1.119 mg H_2O. 3.142 mg substance: 7.331 mg CO_2; 1.060 mg H_2O. 4.001 mg substance: 0.264 ml N_2 (21.5°, 733.0 mm). 1.765 mg substance: 0.116 ml N_2 (21°, 731.6 mm). Found %: C 63.73, 63.63; H 3.88, 3.77; N 7.38, 7.31. $C_{10}H_7O_3N$. Computed %: C 63.49; H 3.70; N 7.41.

8. 2-Phenyloxazole (XI)

a) 0.05 g of 2-phenyloxazole-4-carboxylic acid was placed in a round-bottomed flask filled with water saturated with CO_2 and connected to a gas meter (a buret). Heating resulted in the sublimation of the original acid and the evolution of CO_2, which was most vigorous at 240° (bath temperature). The volume of CO_2 liberated, 5.7 ml, was nearly quantitative (the computed figure is 6 ml).

b) A mixture of 0.1 g of 2-phenyloxazole-4-carboxylic acid and 1 g of previously calcined talc was placed in a Wurtz flask connected to a receiver. One to two drops of a thick, colorless liquid distilled over when the mixture was heated to 240-280°. The liquid was treated with an alcoholic solution of picric acid. The picrate, which separated out as yellow needles, was recrystallized from water. The melting point of the resulting picrate of 2-phenyloxazole was 117-118° [3].

2.182 mg substance: 0.294 ml N_2 (22°, 740.3 mm). Found %: N 15.18. $C_{15}H_9O_8N_4$. Computed %: N 15.01.

SUMMARY

1. Methylation of hippuric ester yields an ester of benzoylsarcosine.

2. Methylation of the diethyl acetal of formyl hippurate yields ethoxymethylene-N-methyl hippurate and the ester of 2-phenyloxazole-4-carboxylic acid, depending upon the reaction conditions.

3. It has been found that ethoxymethylenehippuric ester is formed as an intermediate product in this reaction.

4. It has been learned that the ethoxymethylene groups of ethoxymethylenehippuric ester and of ethoxymethylene-N-methyl hippurate are quite stable against the action of alkalies, but differ sharply in their ability to add alcohol elements, this ability being manifested solely by ethoxymethylenehippuric ester.

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POLAROGRAPHIC INVESTIGATION OF SOME CARDIAC GLYCOSIDES

Yu V Shostenko and the student I Ya Uralova

It is the object of this research to endeavor to extend the number of methods of obtaining a quantitative analysis of cardiac glycosides (in the pure state and as tinctures) by employing a polarographic method.

This is all the more desirable since the results obtained in the analysis of pure cardiac glycosides by the colorimetric method [1], which is the most highly developed one in use at the present time, differ so greatly that biological tests still are the deciding factors.[*] These discrepancies are due to changes that occur in solutions of cardiac glycosides during the colorimetric process itself, as well as to the fact that several sugars and biologically inactive forms of the glycosides yield the same reaction with sodium picrate as do the biologically active cardiac glycosides and their aglucones.

Moreover, polarographic investigations may shed light upon the changes occurring in the medium as well as in the structure of the ions and molecules being reduced. The latter circumstance is quite important in the investigation of such compounds as the cardiac glycosides, on which comparatively little work has been done so far.

The cardiac glycosides have been subjected to polarographic investigation by Herschberg, Wolfe, and Fiser [3]. These authors made a polarographic study of substances in the keto steroid class, as well as of digitoxin, digitoxigenin, convallatoxin, tevetin, and lanatoside "C", as substances whose structure resembles that of the keto steroids. During polarography, all the five foregoing substances were reduced at potentials lying between -1.9 and -2.0 volts against a background consisting of 0.05 N $(C_2H_5)_4NOH$ in 25% isopropyl alcohol, producing waves that were proportional to the concentration. The heights of the polarographic waves of digitoxin and digitoxigenin (the authors cite no data for the other substances they studied) diminish rather appreciably with time, however.

The present paper reports on studies of strophanthidin, cymarin, periplocin, and γ-strophantin.

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[*] In a recent paper F D Zilberg [2] recommends a chemical (colorimetric) method for determining the activity of cardiac glycoside preparations (convaside) combined with the quantitative extraction of the glycosides from their tinctures by adsorption on Al_2O_3; but the general applicability of this method still requires confirmation.

EXPERIMENTAL

The polarographic research was carried out with a photopolarograph made by the Central Institute of Rare Metals (Odessa). The galvanometer used was a mirror galvanometer made by the Physical Institute of Leningrad State University, with a sensitivity of $1.2 \cdot 10^{-9}$ ampere per mm per meter. The distance between the galvanometer mirror and the scale was 500 mm. The mercury used as the cathode was first distilled in vacuum. A new batch of mercury was always used as the bottom electrode. Before beginning the polarography of a fresh solution, the oxygen was driven out by passing hydrogen through the solution for 30 minutes. Hydrogen was passed through for another 7-8 minutes every time a small quantity (0.1-0.2 ml) of the solution undergoing test was added. The hydrogen was produced by electrolysis. The temperature was kept within 18-20° during the tests. The potential of the bottom electrode was measured before and after polarography with respect to a saturated calomel electrode, using a Rapps potentiometer.

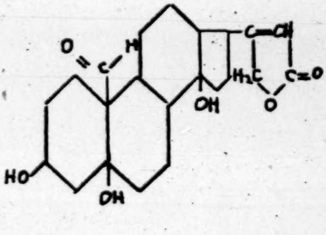
The heights of the polarographic waves was measured by the method of intersecting tangents. The half-wave potentials ($E_{1/2}$) were based on the saturated calomel electrode. The precision of measurement of $E_{1/2}$ was ± 0.03 volt. The pH of the solutions was determined by means of a quinhydrone electrode.

The mercury was dropped into a solution of 0.01 N $(CH_3)_4NI$ in 10% ethanol, with no potential superimposed, at the rate of 1 drop in 4.2 sec; under these conditions $m^{2/3}t^{1/6} = 0.588\ mg^{2/3}\ sec^{-1/2}$.

Aqueous 0.01 N solutions of $(CH_3)_4NI$ and $(CH_3)_4NOH$ were used as the "indifferent" electrolyte, or, as we shall call it henceforth for the sake of brevity, the "background." We employed our modification of the Hofmann synthesis to prepare the $(CH_3)_4NI$. Tetramethylammonium hydroxide was prepared from the synthesized iodide by adding an excess of freshly precipitated silver hydroxide, which had been decanted 30 times, to a concentrated solution of the iodide, which was stirred vigorously. The aqueous solutions were prepared with double-distilled water. The ethyl alcohol used had a b.p. of 78.2°, and its purity was checked polarographically. The glycoside solutions, as well as the "background" solution, were kept in ordinary glass bottles; tests showed that they underwent no change in the course of a month.

We used a sample of crystalline gamma strophantin and samples of cymarin, periplocin, and strophantidin that had been isolated in the phytochemical laboratory of our institute and had been kindly placed at our disposal by D.G.Kolesnikov.

Strophantidin * (I). Because of the poor solubility of strophantidin in water, the initial solution we used was a water-alcohol solution (50% ethyl alcohol by volume) with a concentration of 0.0033 mol of strophantidin per liter. The curve of the reduction of strophantidin is shown in Fig. 1,a. Figure 2 (straight line 1) gives the calibration line for the quantitative determination of strophantidin in a similar medium. When strophantidin is determined quantitatively in water-alcohol solutions, care must be taken that the concentration of the alcohol in the solutions subjected to polarography does not exceed 25-30% by volume, inasmuch as the addition of alcohol, like that of most non-aqueous solvents in general, results in a considerable diminution of the Id [5]. To be able to compare the Id of substances of similar structure, we must possess data obtained in solvent mixtures of the same composition.



(I)

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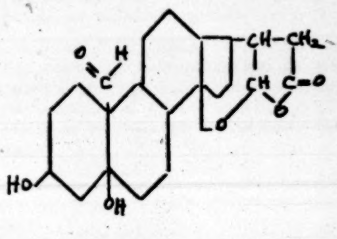
[*] In this and subsequent formulas the structure of the lactone ring is given in the form used in the review by Kanevskaya and Madayeva [4]

We also explored the reduction of strophantidin against a background of 0.01N $(CH_3)_4NOH$. In this case the $E_{1/2}$ of strophantidin is again -1.94 volts. Here the height of the diffusion current waves is somewhat less than in a neutral background, but still can be used to plot calibration lines. The periodic measurement of the diffusion current against the specified background during the course of 24 hours demonstrated that the Id does not vary with time. When the strophantidin was contained in an alkaline medium consisting of 0.03N $(CH_3)_4NOH$, the Id of the strophantidin dropped nearly 60% within 2 hours, compared to the value it had in the neutral background. When this alkaline solution was acidulated, the value of Id rose again, attaining values in the neutral region that are typical of a neutral background. When the alkali concentration was raised to 0.1N, or when the period during which it acted was lengthened (15 hours), the polarographic waves of strophantidin disappear completely. In this case acidulation no longer makes them reappear.

We also investigated the reduction of strophantidin in the acid region. We found that changing the pH of the medium from 6.84 to 3.7 has no effect upon the $E_{1/2}$ of strophantidin, which remains at -1.94 volts. But at a pH of 4.27 the height of the diffusion current wave is already some 20% lower than at a pH of 6.84. At this pH the polarogram exhibits a hydrogen-reduction wave, shifted somewhat toward higher positive values, probably because of the catalytic action of the strophantidin. With further acidulation (pH = 3.7), the height of the wave drops 80%. At a pH of 3.13, the strophantidin wave vanishes, only the hydrogen wave being left. The height of the strophantidin wave is unchanged between the pH values of 7 and 5.1.

We may conclude from the facts set forth above that in an alkaline medium, especially at a high alkali concentration, the strophantidin molecule of, more precisely, that part of it which is reduced at the mercury drop electrode, undergoes changes that render its reduction at the electrode impossible. These changes evidently take place in two steps. The first stage is reversible (the action of acidulation), while the second is not.

According to Jacobs [6], in an alcoholic medium, strophantidin is converted by an alkali with subsequent acidulation, into the so-called isostrophantidin (II).



(II)

Judging by this formula, we may suppose that isostrophantidin will hardly be easy to reduce at a mercury drop electrode, since it lacks the combination of a carbonyl and ethylene bond that favors reduction.

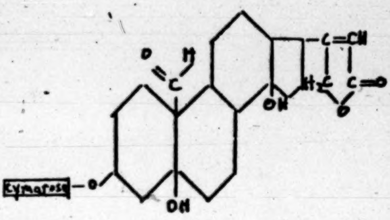
Our experimental data, which disclosed the formation of an irreducible substance from strophantidin as the result of the action of alkali followed by acidulation, confirms this hypothesis and serves, to a certain extent, as proof of the probability of the foregoing formula for isostrophantidin.

Waves of the same height as in the neutral background will, of course, be observed during the acidulation of the alkaline solution of strophantidin until the alkali concentration reaches a value that causes an isoform to appear.

Cymarin (III). This glycoside, which is a derivative of strophantidin, differs from the latter in having a molecule of cymarose attached to C_3 by a glycoside bond. Cymarin is readily soluble in water, which is why we investigated 0.001 to 0.003

molar aqueous solutions. The curve of the reduction of cymarin is given in Fig. 1,b. Fig. 2 gives the calibrating line for the quantitative determination of cymarin.

The maximum error in our quantitative determination does not exceed 10%. The height of the diffusion-current wave for cymarin does not change after the cymarin solution has stood for 20 hours in the electrolyzer with a neutral background and mercury. The pH of cymarin solutions mixed with the background is 6.16.

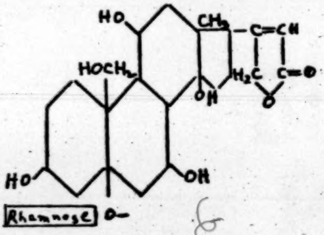


(III)

Gamma strophantin*(IV) is soluble with difficulty in water, and we therefore explored its properties in a 0.003 molar solution in 50% ethyl alcohol (by volume), as in the case of strophantidin.

The curve of the reduction of gamma strophantin is shown in Fig. 1,c.

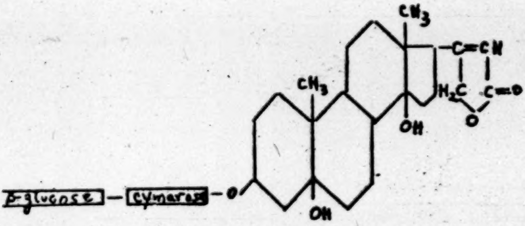
Figure 2 (4 and 5) gives the calibrating lines for the quantitative determination of strophantin. Line 5 applies to a higher percentage of ethyl alcohol in the medium than does line 4, which explains its smaller slope. The maximum error does not exceed 5%. The pH of a solution of gamma strophantine (mixed with the background) = 6.96.



(IV)

Periplocin**(V). The aglucone of periplocin-periplogenin differs from strophantidin in possessing two methyl groups and not having an aldehyde group.

An aqueous 0.003 molar solution was tested. The curve of the reduction of periplocin is shown in Fig. 1,d. The calibrating line for periplocin is given in Fig. 2 (Line 3). The maximum percentage error does not exceed 6.5%.



(V)

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*The tentative formula for the aglucone of gamma strophantin has been taken from the book by L Fiser[e

**The tentative formula for periplocin is taken from the paper by Stoll and Rentz [Helv Chim Acta 22, 1193 ,1939,]

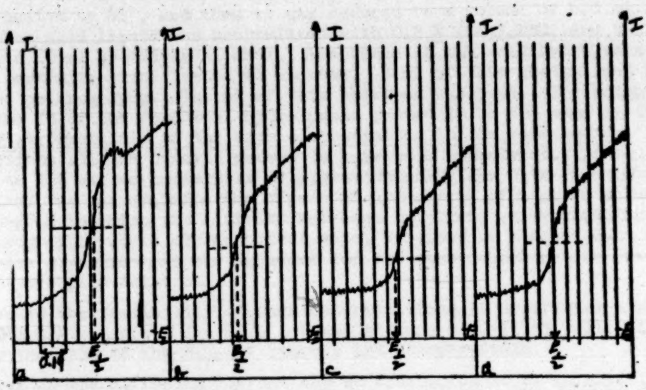

Fig. 1. Curves of the electrolytic reduction of cardiac glycosides. a – Strophantidin: C = 0.0033 mol/liter, sensitivity = 1/50, Id = $6.3 \cdot 10^{-6}$ amp, $E_{1/2}$ = -1.94 volts; b – cymarin: C = 0.001 mol/liter, sensitivity = 1/20, Id = $1.7 \cdot 10^{-6}$ amp, $E_{1/2}$ = -1.90 volts; c – gamma strophantin: C = 0.00077 mol/liter, sensitivity = 1/20, Id = $0.98 \cdot 10^{-6}$ amp, $E_{1/2}$ = -1.95 volts; d – periplocin: C = 0.0008 mol/liter, sensitivity = 1/20, Id = $1.56 \cdot 10^{-6}$ amp, $E_{1/2}$ = -1.96 volts.

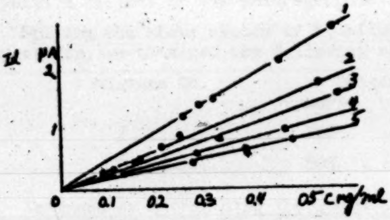

Fig. 2. Calibration lines for the quantitative determination of cardiac glycosides against a background of 0.01 N $(CH_3)_4NI$. 1 – Strophantidin (20-27% ethyl alcohol); 2 – Cymarin (in water; 3 – Periplocin (7.5% ethyl alcohol); 4 – Gamma strophantin (12% ethyl alcohol); 5 – Gamma strophantin (22 % ethyl alcohol).

The Acid Hydrolysis of Cymarin

The acid hydrolysis of the cardiac glycosides by the acids in the gastic juice is encountered when they are administered perorally, and we know from the literature [7] that this hydrolysis results in a weakening of the action of the cardiac glycosides, owing to their cleavage into the less active aglucones and a sugar. According to the same author, in 0.05 N HCl (i.e, in a medium with an acidity approximating that of gastric juice) digitoxin and cymarin are completely hydrolyzed within 24 hours at 34°. Gamma strophantin resists acid hydrolysis better. Inasmuch as cymarin and the corresponding aglucone strophantidin possess different values of Id under identical conditions (medium and concentration), we resolved to utilize this to trace the course of the acid hydrolysis of cymarin by means of polarograms. 2 ml of 0.032 N HCl was added to 10 ml of a 0.0033 molar solution of cymarin in 50% alcohol, the liquid was heated to 66°, and then it was reduced to a volume of 6.0 ml at this temperature. The acid liquid was neutralized with 0.2 $\underline{N}$ $(CH_3)_4NOH$, and the total volume was raised to 10 ml by adding alcohol. The whole of the acid hydrolysis (until the instant of neutralization) lasted 40 minutes. 3 ml of this neutralized hydrolyzate was used for polarography. The pH of this solution was 5.03. The height of the wave and hence the Id of the resultant hydrolyzate proved to be the same as the Id of a solution of strophantidin of the same concentration in the same medium.* Hence, under these conditions all the cymarin proved to have been hydrolyzed. If this procedure is applied to the milder hydrolysis of glycoside solutions with previously determined concentrations, we can evaluate the degree of hydrolysis of a given solution, and hence the degree to which its activity has been impaired, by determining the height of the polarographic waves of the hydrolyzate, provided we possess data on the wave heights of the glycoside and the aglucone for the same concentration as used in the original unhydrolyzed solution.

We checked the feasibility of such determinations in artifiqial mixtures of strophantidin and cymarin. The $E_{1/2}$ of the mixture was -1.945 volts, i.e., it was practically the same as the $E_{1/2}$ of cymarin and strophantidin.

Inasmuch as the diffusion current may be considered to be an additive quantity for substances reduced at the same potential (at least in dilute solutions), the following relationship must hold good:

$$\left.\begin{array}{l} \underline{h}_{\text{mixture}} = \underline{h}_{\text{stroph.}} \cdot X + \underline{h}_{\text{cymarin}} \cdot Y \\ X + Y = 1 \end{array}\right\}$$

where X and Y are the corresponding mol fractions of the solutes, while $\underline{h}_{\text{mixture}}$, $\underline{h}_{\text{stroph.}}$, and $\underline{h}_{\text{cymarin}}$ are the respective heights of the polarographic waves for solutions of equal molarity.

Solving the above system of equations by means of analyzing mixtures of known composition, we obtained the following results:

Mixture No.	Original composition		Found	
	Cymarin	Strophantidin	Cymarin	Strophantidin
1	40%	60%	40%	60%
2	80%	20%	76%	24%

Inasmuch as determining the quantitative proportions in a mixture of glycosides of known composition may be of interest from the practical standpoint, we likewise studied a mixture of 50% gamma strophantin and 50% periplocin by the method outlined above. We found it to contain 51% of gamma strophantin and 49% of periplocin.

The water-alcohol solutions of the glycosides were evaporated to dryness during their treatment, and it is likely that this involves processes that may result in disturbing the structure of the lactone ring. We tested this in the case of strophantidin and gamma strophantin. Here, too, the polarograms of the solutions plotted after the dry residues had been dissolved differed neither in wave height nor in $E_{1/2}$ from the original ones.

The cardiac glycosides are usually associated with saponins in the natural raw material. We therefore ran several experiments to learn what per cent of a saponin may be detected polargraphically (in contrast to a glycoside). We prepared 0.007% and 0.05% aqueous solutions of a saponin. When 4 ml of a 0.007% solution of a saponin is polarographed in a background of 10 ml of 0.01 $\underline{N}$ $(CH_3)_4NI$ + 1 ml of C_2H_5OH at an $\underline{E}$ of -2.13 volts, a high maximum occurs, the origin of which cannot be said to be clear. (A concentration of saponin that is half as strong causes no change in the polarogram of the background). When 1 ml of a 0.05% solution of the saponin is polarographed against the same background, the position of the maximum does not change, but its height becomes considerably greater. When the saponin is added to a solution of gamma strophantin in such a quantity as to constitute 2.4-3% of the glycoside (glycoside concentration = 10^{-4} mol/liter), the height of the glycoside wave begins to drop, and the characteristic maximum makes its appearance. The presence of less than 2% saponin (in terms of the glycoside) does not interfere with the determination of the latter.

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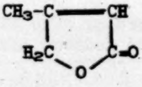
* The $E_{½}$ of the cymarin hydrolyzate was practically identical with the $E_{½}$ for strphantidin.

An endeavor (even though only a qualitative one) to analyze the whole alcoholic tincture of Strophanthus was unsuccessful. A wave corresponding to the reduction of hydrogen could be seen in the polarogram, inasmuch as the pH of this tincture was 5.11. In the region of the potentials where a glycoside wave might have been expected, however, there appeared a maximum of the same type as in the case of the saponin, rendering the determination impossible. Nor did an effort to remove it from the solution with gelatine meet with any success.

Evaluation of Results

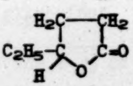
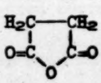
The experiments have shown that all the substances investigated have a practically identical half-wave potential $E_{1/2}$ of -1.95 volts. This indicates that a part of the molecule common to all four substances, namely, the unsaturated lactone ring, is reduced in all four instances. Our value (-1.95 volts) also agrees with the values found by Herschberg and his associates for digitoxin, digitoxigenin, and convallatoxin, which possess the same lactone ring. To provide further proof of this hypothesis, we investigated an aqueous solution of the β-lactone of angelic acid [6] polarographically. Its half-wave potential was found to be -1.96 volts.



(VI)

On the other hand, the fact that the $E_{1/2}$ of the β-lactone of angelic acid is the same as that of the cardiac glycosides is further confirmation of the notion that the lactone ring of the cardiac glycosides is an α,β-unsaturated lactone.

The reduction of the lactone ring in glycosides at a mercury drop electrode speaks against its being considered as an α,β-unsaturated lactone, inasmuch as the configuration of a double bond in a carbonyl group and an ethylenic double bond, which is favorable for polarography, exists only when there is a double bond between the alpha and beta carbon atoms.

Special experiments have convinced us that neither the lactone of ethylvaleric acid  nor succinic anhydride  which possess five-membered rings like that of the β-lactone of angelic acid, but do not have the specified configuration, is reduced above a mercury drop electrode. This fact likewise serves to confirm that an $E_{1/2}$ = -1.95 volts is due precisely to an unsaturated lactone ring, besides pointing to the possibility that products of the isomerization of cardiac glycosides, lacking an unsaturated lactone ring (isostrophantidin, etc.) and hence biologically inactive, will also be inactive polarographically.

The fact that cardiac glycosides are reduced at the same potential enables us to determine the sum of the glycosides. The variable K in the equation $Id = Kc$ is replaced by $\bar{K}$, and from the resulting value of Id we find the concentration, which can be expressed in grams per liter, provided the molecular weights of the constituents are not too far apart; moreover, it is desirable that the K values for the possible constitutents of the mixture be not too far apart.

The identification of the individual pure glycosides on the basis of the differences in their Id values in identical media at various concentrations may well be possible, but it requires great care in operational procedure.

Our experiments and the data in the literature indicate that the reduction of the sugars that may be formed as the result of hydrolysis of the cardiac glycosides does not interfere with the determination of the glycosides, inasmuch as this reduction takes place at much higher concentrations (0.[illegible]N). The fact that the half-wave potentials of various glycosides are practically identical is quite understandable, for the differences in their structure involve either different substituents or different positions of the substituents (including the sugar molecules) in the hydrogenated cyclopentanophenanthrene nucleus, which in turn is merely a substituent for a single atom of hydrogen in the ring being reduced and itself serves rather as a buffer neutralizing the effect of its substituents upon the unsaturated lactone ring.

We know from the data in the literature [8] that the same $E_{1/2}$ is found even for much simpler substances, such as the phenones aurin, cresaurin, and rubrophene, or various fuchsones, though in these cases the substituents are separated from the $>C=O$ group being reduced by only one benzene ring.

We wish to express our gratitude to N.A.Izmailova and D.G.Kolesnikova for their valuable counsel and constant interest in this research.

SUMMARY

1. Volt-ampere curves have been plotted for solutions of strophantidin, cymarin, gamma strophantin, and periplocin, and from these curves the $E_{1/2}$ referred to a saturated calomel electrode, has been determined for these compounds.

2. It has been shown that it is possible to make a quantitative determination of these substances in solutions, and calibrating curves are provided.

3. A new composition of the background has been suggested for the polarography of the glycosides, in which the value of their diffusion current does not change with time.

4. The $E_{1/2}$ of the β-lactone of angelic acid has been determined.

5. The lower limit, above which traces of a saponin interfere with the polarographic determination of the glycosides, has been established.

We have also established the possibility of detecting minute (10^{-8} mol) quantities of the most common impurity in the glycosides - a saponin.

6. A method is suggested for the quantitative determination of the constituents of a glycoside mixture, the qualitative composition and the aggregate concentration of which are known.

7. It has been found that the glycosides are reduced at the same value of $E_{1/2}$ and that, hence, a group that is common to all the glycosides - the unsaturated lactone ring - participates in their reduction, it being highly probable that this ring

has the structure of an α,β-unsaturated lactone.

8. The polarographic method of checking the purity of ampoule solutions of "pure glycosides," as well as of the "pure preparations" themselves, may be recommended as highly sensitive.

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RESEARCHES ON THE DERIVATIVES OF OXAZOLE

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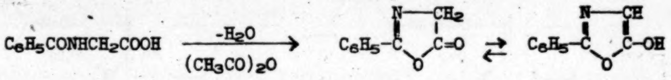
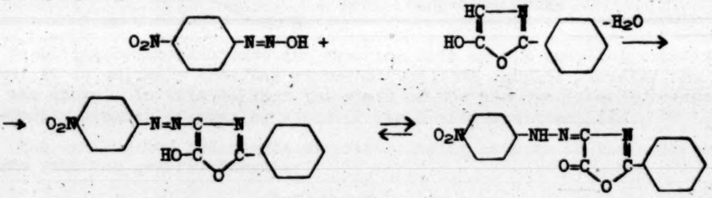
When water was split off from N-benzoylalanine [1] and its homologs by heating them with acetic anhydride, 5-hydroxy-4-methyl-2-phenyloxazole, an unstable, readily hydrolyzed compound, was synthesized. It may be assumed that water can be similarly detached from hippuric acid, yielding 5-hydroxy-2-phenyloxazole:



Like the enols, the latter ought to enter into an azo coupling reaction, yielding stable compounds, stabilized by a developed system of conjugated double bonds.

The present research has confirmed this hypothesis. It has been found that hippuric acid, which is poorly soluble in acetic anhydride, enters solution when heated apparently owing to chemical changes, inasmuch as no precipitate settles out when the solution is cooled. When this solution is diluted with water, oily drops separate out, which are gradually converted into a crystalline mass - hippuric acid, apparently - as the result of hydrolysis of the 5-hydroxy-2-phenyloxazole. When the hippuric acid that had been dissolved in acetic anhydride by heating (i.e., the solution of 5-hydroxy-2-phenyloxazole) is mixed with an aqueous solution of p-nitrobenzenediazohydrate, an azo coupling reaction ensues, producing 4-(p-nitrobenzeneazo)-2-phenyl-5-oxyoxazole:

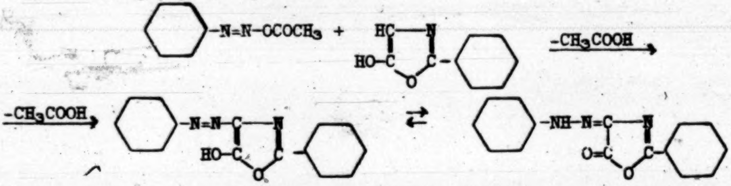


As in other instances of azo coupling with the enols, it is likely that the resulting azo dye is regrouped into a hydrazone. The yield of the azo dye (the hydrazone) is small, inasmuch as the azo coupling is paralleled by hydrolysis of the 5-hydroxy-2-phenyloxazole, giving rise to hippuric acid. Control experiments have shown that the latter does not enter into an azo coupling reaction with p-nitrobenzenediazohydrate or with benzenediazohydrate. The stability of the resulting azo dye (the hydrazone) is due to the presence of a developed system of conjugated double bonds.

No azo coupling results with benzenediazohydrate under analogous conditions, i.e., in an aqueous medium, apparently because the diazo compound is not very active, the hydrolysis reaction taking place much faster than the azo coupling. We succeeded, however, in effecting the azo coupling of 5-hydroxy-2-phenyloxazole with a phenylazo group in a medium of acetic anhydride and acetic acid, using diazoaminobenzene as the reagent. The reaction was carried out by dissolving hippuric acid by heating it in acetic anhydride, cooling the solution, gradually adding diazoaminobenzene, and setting it aside to stand; a few hours later the reaction product settled out as a yellow precipitate. Evidently, the diazoaminobenzene, which does not resist the action of acids, is cleaved by the action of acetic acid and its anhydride:

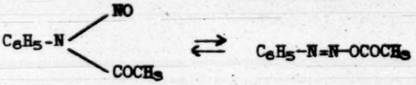
$$C_6H_5{-}N{=}N{-}NH{-}C_6H_5 \xrightarrow{CH_3COOH} C_6H_5{-}N{=}N{-}OCOCH_3 + CH_3CONHC_6H_5 .$$

The resulting diazoacetate enters into an azo coupling reaction, giving rise to 4-benzeneazo-2-phenyl-5-oxyoxazole:



The yield was satisfactory. The acetanilide secured as a by-product was recovered by diluting the mother liquor and was identified by the melting point of a test sample mixed with pure acetanilide as well as by qualitative reactions.

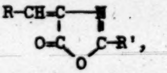
p-Diazoaminotoluene reacts similarly, giving rise to 4-(p-tolueneazo)-2-phenyl-5-oxyoxazole. The azo dye (the hydrazone) formed from diazoaminobenzene and the phenyloxyoxazole can also be produced by mixing a solution of N-nitrosoacetanilide in acetic acid (prepared by nitrosating acetanilide) with a solution of 5-hydroxy-2-phenyloxazole in acetic acid and acetic anhydride, prepared as set forth above. Apparently, the N-nitrosoacetanilide is tautomerized [2]:



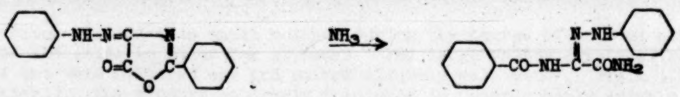
$$C_6H_5{-}N\begin{cases}NO\\COCH_3\end{cases} \rightleftarrows C_6H_5{-}N{=}N{-}OCOCH_3$$

the resulting benzenediazoacetate entering into an azo coupling reaction as outlined above; it is unlikely that the nitrosoacetanilide couples directly, as G.V.Chelintsev [3] has shown. In this variant the yield of the azo dye (the hydrazone) is not high, apparently because of the low yield of the N-nitrosoacetanilide.

The synthesized hydrazones are structurally related to the azlactones [4], compounds with the general formula:

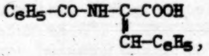


where R and R' are phenyl or some other radical. Like the azlactones, the hydrazones are cleaved by aqueous-alcoholic ammonia, forming colorless crystalline products that resemble the amides:



The present research enables us to reach a conclusion concerning the mechanism of the synthesis of the Erlenmeyer azlactones, which are produced, in the simplest case, by heating hippuric acid, acetic anhydride, benzaldehyde, and sodium acetate together.

Because this azlactone (2-phenyl-4-benzaloxazolinone-5) contained a trace of benzaminocinnamic acid:



$$C_6H_5\text{-CO-NH-}\underset{\underset{\displaystyle CH\text{-}C_6H_5,}{\|}}{C}\text{-COOH}$$

Erlenmeyer [5] believed that first a crotonic type of condensation took place, that acid being formed, followed by cyclization that gives rise to the azlactone. A trace of that acid can be secured as a result of the hydrolysis of the azlactone, however, by washing it with hot water.

The present research proves that heating hippuric acid yields a phenyloxyoxazole, which can enter into further transformations. It is evident that in the synthesis of the azlactones the first step is cyclization, followed by a crotonic condensation.

EXPERIMENTAL

1. Azo coupling of 5-hydroxy-2-phenyloxazole with p-nitrobenzenediazohydrate. 8.95 g of hippuric acid was heated in 20 g of acetic anhydride until it dissolved and then rapidly cooled. Then a solution of p-nitrobenzenediazonium was prepared in the usual manner [6] with 6.9 g of p-nitraniline, and this solution was treated with sodium acetate until it no longer exhibited an acid reaction with Congo. The solution of hippuric acid in acetic anhydride was added drop by drop during the course of 30 minutes at 0° and with constant stirring to the resultant diazo solution. The temperature was maintained by adding bits of ice to the mass. Then the mass was stirred for an hour, and the resultant orange precipitate of the dye was filtered out at 0° and carefully washed with water. The yield was 5 g (32% of the theoretical). The product is nearly insoluble in water, alcohol, ether, acetone, and benzene. Recrystallized from dioxane, it fuses at 317°.

0.129 g substance: 0.2744 g CO_2; 0.0394 g H_2O. 0.1301 g substance: 20.1 ml N_2 (18°, 759.5 mm). Found %: C 57.90; H 3.41; N 17.9. $C_{15}H_{10}O_4N_4$. Computed %: C 58.06; H 3.23; N 18.1.

2. Cleaving 4-(p-nitrobenzeneazo)-2-phenyl-5-oxyoxazole with ammonia. 1.4 g of the substance was mixed with 40 ml of alcohol and 40 ml of 25% ammonia; the mixture was heated over a bath with a reflux condenser until its color disappeared and nearly all of the substance dissolved, after which it was filtered while hot. The colorless crystals that settled out upon cooling were filtered out and washed with water. Yield 1 g (70% of the theoretical). Recrystallized from alcohol or aqueous dioxane, the product melts at 217°.

2.489 mg substance: 0.465 ml N_2 (15°, 739.2 mm). Found %: N 21.62. $C_{15}H_{13}O_4N_5$. Computed %: N 21.81.

3. Azocoupling of 5-hydroxy-2-phenyloxazole with phenyl diazoacetate. a) 2 g of hippuric acid was dissolved by heating it with 10 g of acetic anhydride, and the solution was chilled to 0°. At this temperature and with constant stirring, 2 g of diazo-

aminobenzene was added in small batches during the course of half an hour. The mixture was set aside to stand for 18 hours. The large yellow crystals (scales) that settled out were filtered out and washed slightly with ether. Yield 1.7 g (64% of the theoretical). The product is nearly insoluble in water, poorly soluble in alcohol, and soluble in ether. Recrystallized from methanol, it melted at 202-203°.

0.1873 g substance: 0.4654 g CO_2; 0.0705 g H_2O. 2.370 mg substance: 0.331 ml N_2 (13°, 745.6 mm). Found%: C 67.77; H 4.21; N 16.15. $C_{15}H_{11}O_2N_3$. Computed %: C 67.9; H 4.1; N 15.9.

b) 3.6 g of hippuric acid was dissolved by heating itin 20 g of acetic anhydride after which the solution was chilled to 0°. 2.7 g of acetanilide was dissolved in 20 g of glacial acetic acid, and then 1.5 g of pulverized sodium nitrite was added during the course of half an hour at 0°. The mixture was set aside to stand for an hour and a half at a temperature between 0 and 10°, with constant stirring, and the resulting greenish solution was mixed with the hippuric acid solution at 0° and set aside to stand for 48 hours. The yellow crystals that settled out (0.55 g) were filtered out. Diluting the filtrate with water yielded another 0.22 g; the total was 0.75 g (14% of the theoretical). After recrystallization from methanol, the product did not differ from that synthesized with diazoaminobenzene, either in appearance or in melting point; a mixed test sample exhibited no depression.

4. Azo coupling of 5-hydroxy-2-phenyloxazole with p-tolyl diazoacetate. 2 g of hippuric acid was dissolved in 10 g of acetic anhydride, and the solution was chilled to 0°. At this temperature, 2.25 g of p,p'-diazoaminotoluene was added in small batches during the course of half an hour, with constant stirring. The mixture was set aside to stand for 18 hours. The resulting crystals were filtered out, washed with water, air dried, and recrystallized from benzene. Yield 1.2 g (43 % of the theoretical). Orange crystals ; m.p. 208-209°.

1.944 mg substance: 0.278 ml N_2 (15.5°, 744.4 mm). Found %: N 15.3. $C_{16}H_{13}O_2N_3$. Computed %: N 15.0.

5. Cleavage of 4-benzeneazo-2-phenyl-5-oxyoxazole with ammonia. 1.3 g of 4-benzeneazo-2-phenyl-5-oxyoxazole was mixed with 12 ml of methanol and 12 ml of 25% ammonia; the mixture was heated with a reflux condenser over a bath until its color disappeared and dissolution was complete (about 30 minutes). The solution was filtered while hot; the colorless needles that settled out upon cooling were filtered out and washed with water. Yield 1 g (77% of the theoretical). Recrystallized from methanol, the product melts at 198-199°.

3.66 mg substance: 0.669 ml N_2 (14°, 743.2 mm). Found %: N 21.14. $C_{15}H_{14}O_2N_4$. Computed %: N 19.86.

SUMMARY

1. New azo dyes (hydrazones) containing an oxazole nucleus have been synthesized and their properties described.

2. A conclusion has been drawn from these syntheses concerning the mechanism of the reaction in which azlactones are formed.

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[2] Bamberger, Ber., 27, 914 (1894).
[3] G.V.Chelintsev, Prog. Chem., 14, 266 (1947).
[4] E.Erlenmeyer, Ann., 337, 265 (1904); 284 36 (1895).
[5] E.Erlenmeyer, Ann., 275, 1 (1893); 271, 137 (1892).
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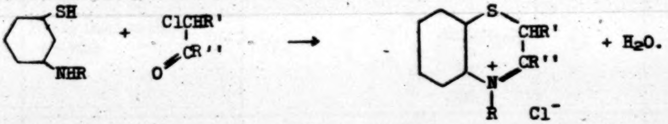
RESEARCHES ON THE DERIVATIVES OF BENZO-1,4-THIAZINE

I. QUATERNARY SALTS OF BENZO-1,4-THIAZINE AND ITS DERIVATIVES

A I. Kiprianov and Z. N. Pazenko

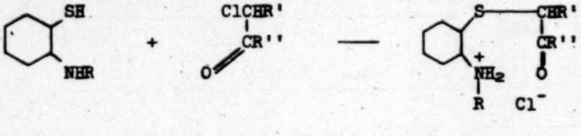
Benzo-1,4-thiazine and its derivatives are extremely weak bases. It is impossible to produce their quaternary salts by the usual methods, say, by heating the bases with alkyl halides or with esters of aryl sulfo acids. That is probably why the quaternary salts of benzo-1,4-thiazine and its derivatives have not been described up to the present time. We have succeeded, however, in demonstrating that these compounds may be readily synthesized by condensing alpha halogen ketones with N-alkyl or N-aryl o-aminothiophenols, as follows:

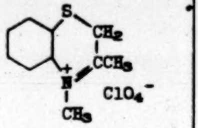
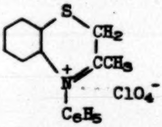
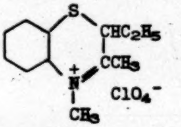
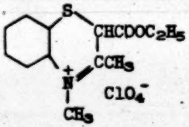
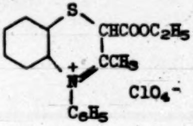
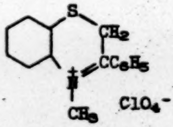
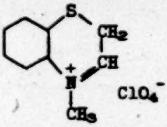


To effect a condensation of this sort, all we have to do is to mix ether or benzene solutions of the constituents in equimolar proportions and heat the mixture until the reaction sets in; the reaction is accompanied by the frothing and clouding of the solution. The thick oil that settles to the bottom of the vessel is washed with benzene, dissolved in alcohol, and treated with a concentrated solution of sodium perchlorate. The quaternary salt that settles out of the solution is purified by recrystallization from alcohol.

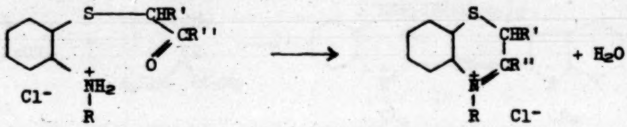
We have synthesized six quaternary salts of benzo-1,4-thiazine in this manner, with various substituents at the 2, 3, and 4 positions; they are listed in the subjoined table (I-VI). These preparations are yellow crystalline substances that decompose at their melting points. They are all soluble in alcohol and acetone, and are hydrolyzed by water. In a powdered state they irritate the mucous membrane of the nose and the eyes.

The condensation of the N-alkyl and the N-aryl aminothiophenols with α-halogen ketones apparently starts at the sulfur atom, giving rise to the chloride of the ester of the aminothiophenol:

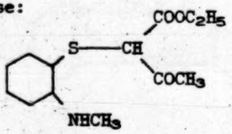


Original substance		Formula of the quaternary salt	Yield, % of theory	Melting point
Halogen ketone	Aminothiophenol			
Chloroacetone	Methylaminothiophenol	(I) 	55	153°
Chloroacetone	Phenylaminothiophenol	(II) 	25	163
α-Chloropropylmethyl ketone	Methylaminothiophenol	(III) 	30	145-147
α-Bromoacetoacetic ester	Methylaminothiophenol	(IV) 	16	167-168
α-Bromoacetoacetic ester	Phenylaminothiophenol	(V) 	28	194-195
ω-Bromoacetophenone	Methylaminothiophenol	(VI) 	41	192-194
1,2-Dibromoethylene	Methylaminothiophenol	(VII) 	12	132

The quaternary salt of benzothiazine is formed in the second phase, involving the detaching of elements of water:



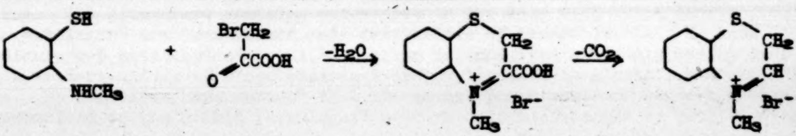
A salt of the aminothio ester can be formed by mixing ether solutions of monochloroacetone and N-methyl- or N-phenyl-o-aminothiophenol at a temperature below 10° and setting the mixture aside to stand in the cold. Within an hour or two a colorless crystalline substance settles out of the solution; heating converts it into a yellow quaternary salt, water being evolved. By condensing N-methyl-o-aminothiophenol with α-bromoacetoacetic ester in benzene, we were able to isolate the following free base:



When heated, the chloride of this thio ester split off water and was cyclized to the chloromethylate of 2-carbethoxy-3-methylbenzothiazine. A similar mechanism had been previously found to exist [1] in the condensation of chloroacetone with thioacetanilide to form the chlorophenylate of 2,4-dimethylbenzothiazole.

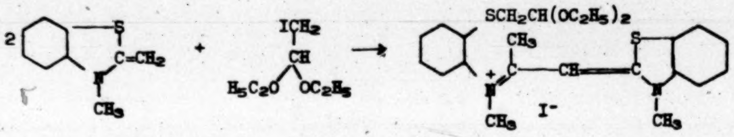
The synthesis of the quaternary salt of benzo-1,4-thiazine itself (VII) was a more complicated problem than synthesizing the quaternary salts of its derivatives. Up to the present time benzo-1,4-thiazine has never been synthesized. Langlet's assertion [2] that he had synthesized benzo-1,4-thiazine as an oil with a b.p. of 238° by boiling o-aminophenylthiol with α,β-dibromoethylene in glacial acetic acid is doubtless based upon an error. The product described by the author as benzo-1,4-thiazine actually was 2-methylbenzothiazole, whose boiling point is 238° and which is readily formed by boiling o-aminothiophenol with acetic acid.

To secure the chloromethylate of benzo-1,4-thiazine, we tried to condense the diethyl acetal of chloroacetaldehyde with N-methyl-o-aminothiophenol, but instead of the quaternary salt we got 2-chloromethyl-3-methylbenzothiazoline. The condensation of bromopyroracemic acid with N-methyl-o-aminothiophenol, which, we thought, should result in the formation of the bromomethylate of benzo-1,4-thiazinecarboxylic acid, yielding the quaternary salt of benzo-1,4-thiazine:

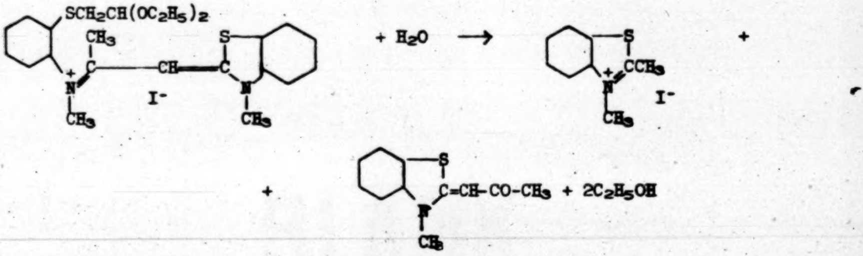


after decarboxylation, did not yield the desired result. The only product recovered from the reaction was the bromomethylate of 2-methylbenzothiazole.

We also tried a Babichev condensation of 2-methylene-3-methylbenzothiazoline with the diethyl acetal of iodoacetaldehyde. According to Babichev [3], reacting methylenic bases of the benzothiazole series with α-halogen ketones yields condensation products, the hydrolysis of which results in acyl methylenic bases and quaternary salts of benzo-1,4-thiazine. The diethyl acetal of iodoacetaldehyde, reacted with 2-methylene-3-methylbenzothiazoline, readily yielded a condensation product, the formation of which should have been represented by the equation:



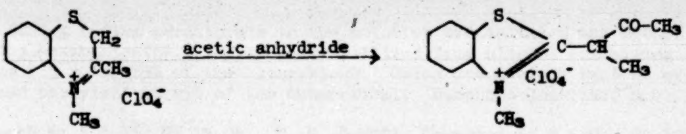
according to the condensation process cited by Babichev and according to the analysis data. But when this yellow condensation product was cleaved with hydrochloric acid, we got – in addition to 2-acetylmethylene-3-methylbenzothiazoline – the iodomethylate of 2-methylbenzothiazole instead of the expected iodomethylate of benzo-1,4-thiazine, apparently because of the isomerization of the thiazine to thiazole.



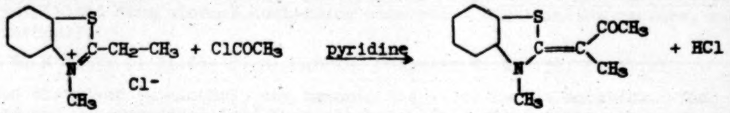
Finally, we succeeded in synthesizing the quaternary salt of benzo-1,4-thiazine by condensing N-methyl-o-aminothiophenol with α,β-dibromoethylene. The reaction was not carried out in acetic acid, as Langlet had done, but by heating the constituents in a xylene solution. The quaternary salt, which was recovered as the perchlorate (with a small yield) exhibited a depression of the melting point when mixed with the methyl perchlorate of 2-methylbenzothiazole, was hydrolyzed quite easily by water, and proved upon analysis to have the composition of the methyl perchlorate of benzo-1,4-thiazine.

As has been set forth above, we repeatedly secured the isomeric quaternary salt, 2-methylbenzothiazole, in our endeavors to synthesize the quaternary salt of benzo-1,4-thiazine. The literature contains references to the ease with which derivatives of benzo-1,4-thiazine are transformed into derivatives of benzothiazole. We know that 2,2-dichloro-3 ketodihydrobenzo-1,4-thiazine is converted extremely easily into the respective derivatives of benzothiazole-2-carboxylic acid by alcohol, ammonia, and amines. We ourselves have noticed that the methyl perchlorate of benzo-1,4-thiazine is isomerized to the methyl perchlorate of 2-methylbenzothiazole by boiling with pyridine.

We have observed transformations of this type, involving the shift of the thiazine ring into a thiazole ring, in other quaternary salts as well. It has been found, for example, that the product that is precipitated when the methyl perchlorate of 3-methylbenzothiazine (m.p. 153°) is boiled in acetic anhydride with pyridine is the methyl perchlorate of 2-[α-acetyl]-ethylbenzothiazole (b.p. 213-215°);



The base recovered from the salt had a m.p. of 118° and exhibited no depression when mixed with the [α-acetyl]-ethylenic base we had synthesized from the chloromethylate of 2-ethylbenzothiazole and acetyl chloride in pyridine:



EXPERIMENTAL

N-Methyl-o-aminothiophenol and N-phenyl-o-aminothiophenol were prepared by cleaving 3-methylbenzothiazolone [4] or 3-phenylbenzothiazolone [5], respectively, with alcoholic caustic potash.

3-Methylbenzothiazine: 6.25 g of the o-aminothiophenol was dissolved in 12 ml of ether and mixed, while chilled, with a solution of 4.6 g of chloroacetone in 10 ml of ether. Slight warming promoted the reaction, which was complete within 10 minutes. The reddish oil that settled changed into a yellow crystalline mass upon standing. The crystals were filtered out, washed with alcohol and ether, and recrystallized from alcohol. 3-Methylbenzothiazine chloride has a m.p. of 141-142° with decomposition. The yield was 90% of the theoretical.

In order to recover the base, the chloride was treated with an aqueous solution of ammonia, the base settling out as a light cream-colored powder. It was purified by reprecipitation with ligroin from benzene. M.p. 52°.

Found %: N 8.69. C_9H_9NS. Computed %: N 8.58.

The base forms rather unstable salts, which are soluble with difficult in water, when reacted with sulfuric and perchloric acids. Aqueous solutions of the salt hydrolyze.

Methyl perchlorate of 3-methylbenzothiazine (I). When 3-methylbenzothiazine is heated with ethyl iodide, diethyl sulfate, or the ethyl ester of p-toluenesulfonic acid, the solution darkens at 60°, and complete tarring occurs with a further rise in temperature. When equimolar proportions of the base and of freshly distilled dimethyl sulfate were heated to 80° for 20 minutes in a sealed tube, we succeeded in recovering the quaternary salt of 3-methylbenzothiazine in the form of the perchlorate, with a m.p. of 151-153° (yield 3% of the theoretical). The same salt is synthesized incomparably more simply in the following manner.

4 g of N-methyl-o-aminothiophenol in 10 ml of anhydrous benzene was mixed, with chilling, with 2.9 g of chloroacetone in 5 ml of benzene. The mixture was warmed slightly until the benzene began to boil; this gave rise to a vigorous reaction, with the evolution of heat and the settling out of a brown oil. The reaction ceased after 10-15 minutes, and the oil solidified into a crystalline mass, which was carefully washed with benzene or ether to remove the initial substances. The salt was dissolved in water, separated from the insoluble tarry impurities, and concentrated to a volume

of 3-4 ml. Adding sodium perchlorate to the solution precipitated the methyl perchlorate of 3-methylbenzothiazine. It was recrystallized from alcohol containing charcoal. The yield was 4.3 g, or 55% of the theoretical. Using iodoacetone instead of chloroacetone raised the yield to 65% of the theoretical. Lustrous lamellae, m.p. 153° (with decomp.).

Found %: N 5.16; Cl 13.04. $C_{10}H_{12}O_4NSCl$. Computed %: N 5.04; Cl 12.77.

0.5 g of the methyl perchlorate of 3-methylbenzothiazine (I), 2.5 ml of acetic anhydride, and 5 drops of pyridine were heated for an hour with a reflux condenser. The fine yellow needles that settled out of the solution upon cooling were filtered out and washed with the anhydride and with benzene; they weighed 0.25 g. The substance was doubly recrystallized from alcohol containing charcoal. Light yellow needles, m.p. 213-215° (with decomp.).

Found %: N 4.37; Cl 11.04; $C_{12}H_{14}O_5NClS$. Computed %: N 4.39; Cl 11.11.

The salt was dissolved in alcohol, and ammonia was added to the solution. The base that settled out was recrystallized from alcohol. Fine silky yellowish needles with a m.p. of 117-119°. A test sample, mixed with 2-α-acetylethylidene-3-methylbenzothiazoline (vide infra), exhibited no depression.

2-(α-Acetyl)-ethylidene-3-methylbenzothiazoline. 0.8 g (1.5 mol) of acetyl chloride was added, with constant stirring and effective chiling, to a solution of 1.5 g of the chloromethylate of 2-ethylbenzothiazole in 5 ml of anhydrous pyridine. Half an hour later the solution was heated to 100° for 15 minutes. Then the pyridine was driven off in vacuum, and the residue was heated with water. The resulting precipitate was filtered out, air dried, and recrystallized from ligroin. Slightly yellowish needles, m.p. 118-119°.

Found %: N 6.56; S 14.32. $C_{12}H_{13}ONS$. Computed %: N 6.39; S 14.65.

The picrate of the bases consisted of beautiful yellow needles with a m.p. of 146°. The perchlorate consisted of yellowish needles with a m.p. of 214-215° (with decomp).

Phenyl perchlorate of 3-methylbenzothiazine (II). 2 g of N-phenyl-o-aminothiophenol in 3 ml of benzene was mixed with 0.93 g (1 mol) of chloroacetone in 2 ml of benzene, and then heated over a water bath for 5 minutes. After it had cooled, the reaction mixture was diluted with twice its volume of benzene, and the reddish oil that settled out was washed with benzene and dissolved in 6 ml of aqueous alcohol. The tarry impurities were extracted with benzene, and sodium perchlorate was added to the filtered solution. The perchlorate precipitate was recrystallized from alcohol. Yield 0.9 g, or 25% of the theoretical. Dilute aqueous solutions of the salt undergo hydrolysis, a base with a m.p. of 83° being precipitated. The phenyl perchlorate bursts into flame when rapidly heated, though the melting point (163° with decomp.) can be determined by heating it slowly.

Found %: N 4.05; Cl 10.70. $C_{15}H_{14}O_4NSCl$. Computed %: N 4.13; Cl 10.45.

Methyl perchlorate of 2-ethyl-3-methylbenzothiazine (III). The initial chloroketone - 3-chloropentanone-2 - was synthesized from methyl propyl ketone by chlorinating it with chlorine diluted with carbon dioxide [8]. 1.4 g of N-methyl-o-aminothiophenol dissolved in 3 ml of benzene was mixed in the cold with 1.1 g of 3-chloropentaneone-2 dissolved in 3 ml of benzene. The mixture was heated over a water bath for 10 minutes. The process of recovery and refining was the same as in the preceding cases. Yield 0.9 g, or 30% of the theoretical. Light yellow needles that fuse at 145-147° (with decomp.).

Found %: N 4.38. $C_{12}H_{16}O_4NSCl$. Computed %: N 4.59.

Methyl perchlorate of 2-carbethoxy-3-methylbenzothiazine (IV). α-Bromoacetoacetic ester was prepared by the Conrad and Schmidt method [7]. A mixture consisting of 1.4 g of N-methyl-o-aminothiophenol in 3 ml of benzene plus 2.1 g of α-bromoacetoacetic ester in 2 ml of benzene was heated for 10 minutes over a water bath. The oil that settled out was separated from the benzene layer (see below for the investigation of the benzene layer), washed with benzene, and dissolved in water. The quaternary salt was precipitated from the transparent aqueous layer by $NaClO_4$. Recrystallization from alcohol yielded 0.65 g, or 19% of the theoretical. Yellow needles, m.p. 167-168° (with decomp.).

Found %: N 3.89; Cl 9.89. $C_{13}H_{16}O_6NSCl$. Computed %: N 4.01; Cl 10.01.

2-Methylaminophenyl-α-mercaptoacetoacetic ester. After the chloromethylate of 2-carbethoxy-3-methylbenzothiazine had been recovered, the benzene solution was concentrated over a water bath. After 12 hours of standing, 0.8 g of crystals was recovered from the solution; after crystallization from alcohol containing charcoal, they consisted of colorless lamellae with a m.p. of 168° (with decomp.). The compound contains no halogen nor does it condense with p-dimethylaminobenzaldehyde or with the orthoacetate in acetic anhydride.

Found %: N 5.28; $C_{13}H_{17}O_3NS$. Computed %: N 5.24.

When a current of anhydrous hydrogen chloride is passed through a chilled solution of the preparation in benzene, an unstable hydrochloride settles out. Heating the hydrochloride for half an hour to 60° in a sealed tube results in the evolution of water, and the substance fuses. The reaction product was dissolved in water and treated with sodium perchlorate. The perchlorate settled out; it fused at 166-168° with decomposition and exhibited no depression when mixed with the methyl perchlorate of 2-carbethoxy-3-methyl-benzothiazine.

Phenyl perchlorate of 2-carbethoxy-3-methylbenzothiazine (V). The preparation was synthesized from 2 g of N-phenyl-o-aminothiophenol and 2.1 g of bromoacetoacetic ester by the preceding method. Recrystallization from absolute alcohol resulted in a yield of 0.98 g, or 28% of the theoretical. Light-yellow platelets, m.p. 194-195° (with decomp.).

Found %: N 3.54. $C_{18}H_{18}O_6NSCl$. Computed %: N 3.41.

The salt is readily hydrolyzed by water and even by aqueous alcohol.

Methyl perchlorate of 3-phenylbenzothiazine (VI). This was synthesized from 2 g of N-methyl-o-aminothiophenol and 2.86 g of ω-bromoacetophenone in toluene by the method used previously. It was purified as in the preceding tests. The yellow crystalline salt had a m.p. of 192-194° (with decomp.) after recrystallization from alcohol. Yield 2 g, or 41% of the theoretical.

Found %: N 4.08; Cl 10.37. $C_{15}H_{14}O_4NSCl$. Computed %: N 4.11; Cl 10.45.

Methyl perchlorate of benzothiazine (VII). 2.8 g of N-methyl-o-aminothiophenol dissolved in 6 ml of xylene and 3.7 g of α,β-dibromoethylene dissolved in 3 ml of xylene were mixed together in the cold and then heated to 40-50° for 2 hours. The oil that settled out was separated, washed with benzene and ether, and dissolved in aqueous alcohol. A solution of sodium perchlorate was added to the transparent filtered solution. Oil settled out again, and it was dissolved in alcohol, treated with activated charcoal, and chilled. This time crystals settled out; they were suction-filtered and washed with alcohol. Yield 0.63 g, or 12% of the theoretical. Light yellow needles, m.p. 132° (with decomp.).

Found %: N 5.18; Cl 13.66: $C_9H_{10}O_4NSCl$. Computed %: N 5.32; Cl 13.47.

A test sample, mixed with the methyl perchlorate of 2-methylbenzothiazole, exhibited a depression of 12°.

0.2 g of the methyl perchlorate of benzothiazine was dissolved in 1 ml of pyridine, and the solution was boiled for 10 minutes with a reflux condenser, after which it was diluted with water and treated with 1 ml of 33% perchloric acid. A salt was thrown down, which was washed with water and recrystallized from alcohol. This yielded 0.09 g of minute colorless needles with a m.p. of 124°. A test sample, mixed with the methyl perchlorate of 2-methylbenzothiazole, exhibited no depression.

SUMMARY

A general method is suggested for the synthesis of the hitherto unknown quaternary salts of derivatives of benzo-1,4-thiazine, involving the condensation of α-halogen ketones with N-alkyl or N-aryl orthoaminothiophenols. Six methyl and phenyl perchlorates of derivatives of benzo-1,4-thiazine have been synthesized in this manner. The methyl perchlorate of benzo-1,4-thiazine itself was synthesized by condensing N-methyl-o-aminothiophenol with symmetrical dibromoethylene.

It has been shown that the quaternary salts of benzo-1,4-thiazine and its derivatives are readily isomerized to the corresponding quaternary salts of 2-alkyl benzothiazoles.

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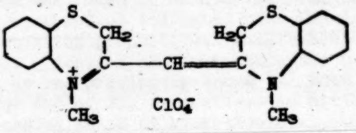
RESEARCHES ON THE DERIVATIVES OF BENZO-1,4-THIAZINE

II. CYANIN DYESTUFFS OF THE BENZO-1,4-THIAZINE SERIES

A. I. Kiprianov and Z. N. Pazenko

No cyanin dyes containing the benzo-1,4-thiazine nucleus are known, except for one asymmetrical monomethynecyanin described in Beilenson's patent [1]. We have developed a method for synthesizing the quaternary salts of benzo-1,4-thiazine and its derivatives [2]. These salts condense readily, resulting in the formation of cyanin dyes. The synthesis and the properties of the thiazinecyanins we have produced are described below.

We synthesized a symmetrical monomethyne dye:

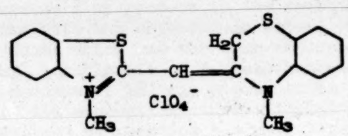


(I)

Absorption maximum: 495 mμ

by boiling an alcoholic solution of the methyl perchlorate of 3-methylbenzothiazine and methyl methosulfate in the presence of anhydrous sodium acetoacetate.

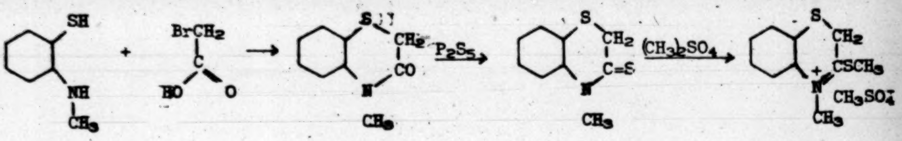
The known asymmetrical monomethynecyanin:



(II)

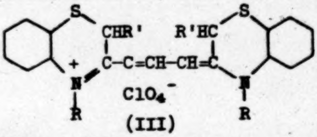
Absorption maximum: 485 mμ

was synthesized in two ways: by condensing the methyl perchlorate of 3-methylbenzo-1,4-thiazine with the methyl methosulfate of 2-methylmercaptobenzothiazole, and by condensing the methyl methosulfate of 2-methylbenzothiazole with the methyl methosulfate of 3-methylmercaptobenzothiazine. The latter compound was synthesized as follows:



The monomethynecyanins that contain a benzothiazine nucleus are orange-red crystalline sybstances that are decolorized when an alcoholic solution of an alkali is added to them.

To synthesize thiazinecarbocyanins (III), we boiled solutions of the quaternary salts of 3-methylbenzothiazine and of its derivatives with the orthoformic ester in acetic anhydride to which pyridine had been added. We found that two dyestuffs - one red, and the other purple - are produced simultaneously from the quaternary salts of 3-methylbenzo-1,4-thiazine. Analysis indicated that these two dyes had the identical composition, that of thiazinecarbocyanin. It was also found that the quaternary salts of unsubstituted benzo-1,4-thiazine and 3-phenylbenzo-1,4-thiazine, which do not have the reactive methyl group in the 3 position, yield dyes nevertheless when condensed with the orthoformic ester.

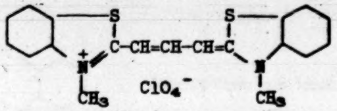
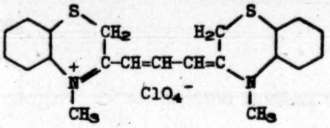
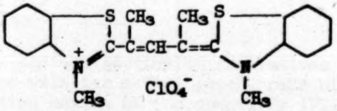
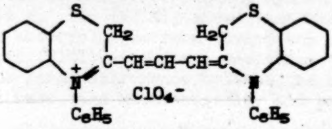
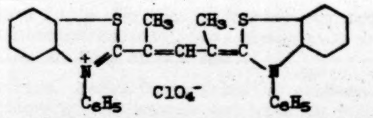
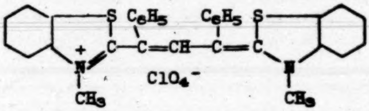
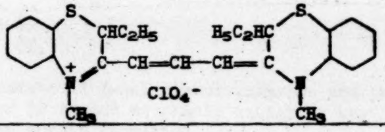
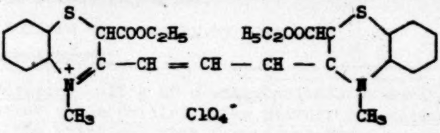


(III)

At first we thought that one quaternary salt yielded two isomeric thiazinecarbocyanins as the result of condensations that occurred at the methylene group at the 2 position of the thiazine ring as well as at the methyl group at the 3 position. In fact, we subsequently succeeded in proving the reactivity of this methylene group and its ability to condense with aldehydes [3]. But in the reaction with the orthoformic ester the reason for the formation of two isomeric dyes was found to be not the reactivity of the methylene group. Research on the dyes synthesized indicated that the synthesis of thiazinecarbocyanin, the normal condensation product, was paralleled by the synthesis of an isomeric thiacarbocyanin, - i.e., a dye that contained benzothiazole nuclei instead of benzothiazine ones. We had previously shown [2] that boiling the quaternary salts of benzo-1,4-thiazine and of its derivatives in pyridine promotes their isomerization into the corresponding salts of benzothiazole.

The purple dyestuff with an absorption maximum at 570 mμ, secured as a by-product in the condensation of the methyl perchlorate of 3-methylbenzothiazine with the orthoformic ester, proved to be identical with 8,10-dimethylthiacarbocyanin, which had been synthesized by Kiprianov and Ushenko [4] from the orthoformic ester and a quaternary salt of 2-ethylbenzothiazole. The dyestuff with an absorption maximum of 600 mμ formed as a by-product in the reaction of the phenyl perchlorate of 3-methylbenzothiazine with the orthoformic ester, proved to be N,N-diphenyl-8,10-dimethylthiacarbocyanin, which has the same absorption maximum [4]. The condensation product of the methyl perchlorate of 3-phenylbenzothiazine and the orthoformic ester, with an absorption maximum of 581 mμ, proved to be identical in its absorption maximum and in the shape of its absorption curve with 8,10-diphenylthiacarbocyanin [4]. Lastly, the dyestuff produced by reacting the methyl perchlorate of unsubstituted benzothiazine with the orthoformic ester proved to be the simplest thiacarbocyanin, with an absorption maximum at 558 mμ. The table gives the formulas and the absorption maxima in an alcoholic solution of the thiazinecarbocyanins we have synthesized and of the isomeric thiacarbocyanins formed at the same time.

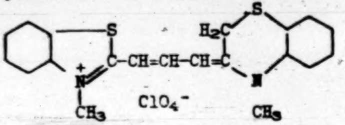
As the table indicates, the absorption maxima of the thiazinecarbocyanins lie in

Original quaternary salt	Products of its condensation with the orthoformic ester, and the respective absorption maxima		
Methyl perchlorate of benzothiazine			558 mμ
Methyl perchlorate of 3-methylbenzothiazine	(IV)		528 mμ
			570 mμ
Phenyl perchlorate of 3-methylbenzothiazine	(V)		536 mμ
			600 mμ
Methyl perchlorate of 3-phenylbenzothiazine			580 mμ
Methyl perchlorate of 2-ethyl-3-methylbenzothiazine	(VI)		548 mμ
Methyl perchlorate of 2-carboxyethyl-3-methyl benzothiazine	(VII)		554 mμ

a shorter wavelength region than the maxima of the thiacarbocyanins. This may be due either to a disturbance of the conjugation of the polymethyne chains with the sulfur atom in the thiazine ring, or to the weak basic properties of benzothiazine compared to benzothiazole.

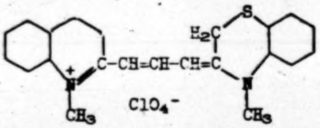
Two asymmetrical carbocyanins:

(VII)



Absorption maximum 532 mμ

(VIII)



Absorption maximum 543 mμ

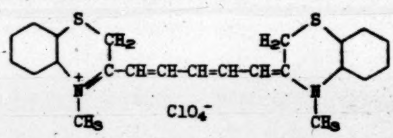
were synthesized by condensing the ω-acetanilidovinylic derivatives of the iodomethylates of benzothiazole and quinoline with the methyl perchlorate of 3-methylbenzothiazine. Comparison of the absorption maxima of the dyestuffs (VII) and (VIII) with the mean value of the absorption maxima of the corresponding symmetrical dyes [528 and 558 mμ for (VII) and 528 and 606 mμ for (VIII)] shows that the dyestuff (VII) exhibits a deviation (a shift of the absorption maximum toward the shorter wavelengths) of 11 mμ, while the dyestuff (VIII) exhibits a deviation of 24 mμ. These deviations are due, evidently, to the large difference between the basic properties of benzothiazine, an extremely weak base, and benzothiazole, and particularly quinoline.

Beilenson and Hamer have described [5] a dye that resembles our preparation (VII), but containing the benzo-2,4-thiazine nucleus. Its absorption maximum of 530 mμ is almost the same as the absorption maximum of our dye.

Efforts to synthesize an asymmetrical carbocyanin from the quaternary salts of 3-methylbenzothiazine and ω-acetanilidovinylbenzoxazole met with no success. The only reaction products found were symmetrical dyestuffs – hydroxycarbocyanin and 8,10-dimethylthiacarbocyanin.

Thiazinedicarbocyanin:

(IX)



Absorption maximum: 634 mμ

was synthesized from the methyl perchlorate of 3-methylbenzothiazine and the anilanilide of malonic dialdehyde. The dye is formed extremely easily by heating the constituents slightly for one minute in acetic anhydride.

All the thiazinecyanins are decolorized very easily by alkalies.

EXPERIMENTAL

4-Methyl-3-oxodihydrobenzo-1,4-thiazine. 15 g of o-methylaminothiophenol and 15 g of bromoacetic acid were mixed together while chilled. The mixture was allowed to stand for 1 hour at room temperature; the thick oil that formed was first treated with a soda solution and then comminuted in a mortar with a 2N solution of hydrochloric acid. The solidified mass was filtered out, washed on the filter with dilute hydrochloric acid, and dried. The yield of unrefined 4-methyl-3-oxodihydrobenzo-1,4-thiazine was 14.5 g, or 75% of the theoretical. After triple recrystallization from petroleum ether, the preparation fused at 55-56° and distilled at 156° at 15 mm with slight decomposition. Colorless, lustrous platelets.

Found %: N 7.78. C_9H_9ONS. Computed %: N 7.82.

The preparation is soluble in most organic solvents. It possesses extremely weak basic properties.

4-Methyl-3-thiodihydrobenzo-1,4-thiazine. 13.5 g of N-methyloxodihydrobenzothiazine was comminuted in a mortar with 10 g of phosphorus pentasulfide. The resulting liquid mass was transferred to a beaker and boiled for 15 minutes, with stirring, with 30 ml of toluene. When the melt began to turn brown, the toluene solution was decanted, and the residue was twice retreated with fresh batches of toluene, using 10 ml each time. Crystals of the thione settled out of the combined toluene extracts when they cooled. They were filtered out and recrystallized from toluene. Yield 2.2 g, or 15% of the theoretical. The thione has a m.p. of 45-46°, is colored golden yellow, and is insoluble in alkalies and acids in the cold.

Found %: N 7.31. $C_9H_9NS_2$. Computed %: N 7.18.

Methyl methosulfate of 3-methylmercaptobenzo-1,4-thiazine. 1.3 g of dimethyl sulfate was added to 2 g of 4-methyl-3-thiodihydrobenzo-1,4-thiazine. A homogenous mixture was formed, which evolved considerable heat. It was heated for 1 hour at 100°, and the resulting dark-brown mass was washed with benzene and ether and dried in an exsiccator. A light-brown hygroscopic mass.

(3-Methylbenzothiazole-2)-(4-methylbenzo-1,4-thiazine-3)-monomethynecyanin perchlorate. a) 0.3 g of the methyl perchlorate of 3-methylbenzothiazine, 0.34 g of the methyl methosulfate of 2-methylmercaptobenzothiazole, and a small quantity of fused sodium acetate in 3 ml of absolute alcohol were heated to boiling for 1 hour. The red precipitate that was thrown down was recrystallized from alcohol. M.p. 168° with decomposition. A dark-red powder; absorption maximum in alcoholic solution: 485 mμ.

Found %: S 14.73. $C_{18}H_{17}N_2S_2ClO_4$. Computed %: S 15.09.

b) 0.5 g of the methyl methosulfate of 3-methylmercaptobenzothiazine, 0.4 g of the methyl methosulfate of 2-methylbenzothiazole, and 0.2 g of sodium acetate were heated for 15 minutes in 5 ml of absolute alcohol. The precipitate was washed on the filter and recrystallized from alcohol. It was the same as the preparation produced by Method a).

Bis-(4-methylbenzo-1,4-thiazine-3)-monomethynecyanin perchlorate (I). 0.5 g of the methyl methosulfate of 3-methylmercaptobenzothiazine, 0.4 g of the methyl perchlorate of 3-methylbenzothiazine, and 0.2 g of anhydrous sodium acetate in 3 ml of absolute alcohol were boiled for 15 minutes over a water bath. After cooling the solution was diluted with ether, and the precipitate was filtered out and recrystallized from glacial acetic acid. Yield 0.13 g; absorption maximum 495 mμ.

Found %: S 14.74. $C_{19}H_{19}N_2S_2ClO_4$. Computed %: S 14.72.

Condensation of the methyl perchlorate of benzo-1,4-thiazine with orthoformic ester. Qualitative tests proved that a quaternary salt of benzothiazine does not form a dyestuff with orthoformic ester in acetic anhydride. When it is heated with the orthoformic ester in pyridine or in acetic anhydride to which pyridine has been added, the solution gradually turns raspberry-red and the thiacarbocyanin is formed. Gray crystals with a metallic luster; absorption maximum at 558 mμ. Yield from 0.2

g of the quaternary salt: 0.01 g.

Found %: N 6.55. $C_{19}H_{17}O_4S_2N_2Cl$. Computed %: N 6.48.

Bis-(4-methylbenzo-1,4-thiazine-3)-trimethynecyanin perchlorate (III). 1 g of methyl perchlorate of 3-methylbenzo-1,4-thiazine, 1 ml of the ester of orthoformic acid, and 5 g of acetic anhydride were heated to 50-60° for 20 minutes. The bright-red solution was diluted with 30 ml of ether, and the red precipitate was recrystallized from ether and dried at 80°. Yield 0.1 g, or 12% of the theoretical. M.p. 176° with decomposition. Absorption maximum: 528 mμ.

Found %: N 6.23; S 13.73; Cl 7.17. $C_{21}H_{21}O_4N_2S_2Cl$. Computed %: N 6.05; S 13.79; Cl 7.34.

When the methyl perchlorate of 3-methylbenzothiazine is condensed with the ester of orthoformic acid in pyridine or in acetic anhydride to which pyridine has been added, instead of in straight acetic anhydride, the principal reaction product (with a yield of 16-20% of the theoretical after recrystallization from alcohol) is a thiacarbocyanin - bis-(3-methylbenzothiazole-2)-8,10-dimethyltrimethynecyanin perchlorate, a crystalline purple powder, m.p. 189-191° with decomposition; absorption maximum 570 mμ.

Found %: S 14.08; N 5.97; Cl 7.08. $C_{21}H_{21}O_4N_2S_2Cl$. Computed %: S 13.79; N 6.05; Cl 7.34.

A small quantity of a thiazinecarbocyanin with a m.p. of 173-176° (with decomposition) and an absorption maximum of 528 mμ can be precipitated by ether from the mother liquor.

Bis-(4-phenylbenzo-1,4-thiazine-3)-trimethynecyanin perchlorate (IV). 0.5 g of the phenyl perchlorate of 3-methylbenzothiazine, 1 ml of acetic anhydride, 1 ml of the ester of orthoformic acid, and a few drops of pyridine were heated to boiling for 10 minutes. Upon cooling 0.2 g of a dyestuff was recovered, which proved to be a thiacarbocyanin - bis-(3-phenylbenzothiazole-2)-8,10-dimethyltrimethynecyanin perchlorate, which has the same absorption curve and the same maximum at 600 mμ as the preparation described by Kiprianov and Ushenko [4]. Platelets with a golden lustre; m.p. approx. 230° with decomposition.

Found %: N 4.76. $C_{31}H_{25}O_4N_2S_2Cl$. Computed %: N 4.60.

The mother liquor was treated with ether after the foregoing dye had been secured. This yielded a small quantity of precipitate of a dye that was recrystallized from alcohol. It proved to be less soluble in alcohol than the thiacarbocyanin synthesized as the principal product. The nature of the absorption curve (a wide band) and its behavior toward alkalies (ready decolorization) indicate that this preparation is fundamentally different from a thiacarbocyanin. Yield 0.08 g. Crystals with a golden luster; absorption maximum 536 mμ.

Found %: N 4.42. $C_{31}H_{25}O_4N_2S_2Cl$. Computed %: N 4.60.

Bis-(2-ethyl-4-methylbenzo-1,4-thiazine-3)-trimethynecyanin perchlorate (V). 0.5 g of the methyl perchlorate of 2-ethyl-3-methylbenzothiazine, 1 ml of the ester of orthoformic acid, and 3 ml of acetic anhydride were boiled for 10 minutes. A golden powder separated out upon cooling. It was recrystallized from alcohol. Yield 0.22 g, or 52% of the theoretical. Golden needles, m.p. 273° with decomposition. Absorption maximum 548 mμ.

Found %: N 5.21; S 12.02. $C_{25}H_{29}O_4N_2S_2Cl$. Computed %: N 5.38; S 12.30.

Bis-(2-carbethoxy-4-methylbenzo-1,4-thiazine-3)-trimethynecyanin perchlorate (VI). 0.5 g of the methyl perchlorate of 2-carbethoxy-3-methylbenzothiazine, 1 ml of the ester of orthoformic acid, and 3 ml of acetic anhydride to which 3 drops of pyridine had been added were boiled for 10 minutes. The dye was first recovered as an amorphous mass with a golden luster, but it was secured as golden crystalline lamellae with a m.p. of more than 300° after recrystallization from alcohol. Absorption maximum 554 mμ.

Found %: N 4.94. $C_{27}H_{29}O_8N_2S_2Cl$. Computed %: N 4.61.

Bis-(3-methylbenzothiazole-2)-8,10-diphenyltrimethynecyanin perchlorate. 1 g of the methyl perchlorate of 3-phenylbenzothiazine and 2 ml of the ester of orthoformic acid were heated for 10 minutes with acetic anhydride. No color appeared. When pyridine was added to the solution, the solution turned purple, but further boiling clearly resulted in the decomposition of the dye that was formed. It was therefore precipitated from the solution together with the unreacted quaternary salt by means of ether. We were unable to secure the dye in the pure state. Purple crystals; absorption maximum 581 mμ.

(4-Methylbenzo-1,4-thiazine-3)-(3-methylbenzothiazole-2)-trimethynecyanin perchlorate (VII). 0.5 g of the methyl perchlorate of 3-methylbenzothiazine, 0.75 g of the iodomethylate of ω-acetanilidovinylbenzothiazole, and 1 g of anhydrous sodium acetate were boiled with 10 ml of acetic anhydride for 15 minutes. After the mixture had cooled, the crystalline precipitate was filtered out and washed with acetic anhydride, alcohol, and ether. Yield 0.54 g or 73% of the theoretical. After recrystallization from a small amount of alcohol, the preparation was a dark-purple crystalline powder. Absorption maximum 532 mμ. An alcoholic solution of the dye turned orange when a few drops of ammonia were added.

Found %: S 14.29: $C_{20}H_{19}O_4N_2S_2Cl$. Computed %: S 14.22.

(4-Methylbenzo-1,4-thiazine-3)-(1-methylquinoline-2)-trimethynecyanin perchlorate (VIII). 0.3 g of the methyl perchlorate of 3-methylbenzothiazine, 0.43 g of the iodomethylate of 2-ω-acetanilidovinylquinoline (m.p. 265°, iodine found, %: 29.78; iodine computed, %: 29.53), and 0.35 g of anhydrous sodium acetate in 1.4 ml of acetic anhydride were heated for 10 minutes over a water bath. The dye that separated out upon cooling was recrystallized from acetic anhydride. Yield 0.12 g of a dark-purple, finely crystalline powder. An alcoholic solution is decolorized by ammonia and by weak alkalies, but not instantaneously. Absorption maximum 542 mμ.

Found %: N 6.28; S 6.89. $C_{22}H_{21}O_4N_2SCl$. Computed %: N 6.29; S 7.19.

Bis-(4-methylbenzo-1,4-thiazine-3)-pentamethynecyanin perchlorate (IX). 0.5 g of the methyl perchlorate of 3-methylbenzothiazine and 2.5 g of anilanilide hydrochloride of malonic dialdehyde in 5 ml of acetic anhydride to which 3 drops of pyridine had been added were boiled together for 1 minute. The blue crystalline precipitate was recrystallized from alcohol. Yield 0.25 g, or 57% of the theoretical. Dark-blue needles with a copper sheen. Absorption maximum 634 mμ.

Found %: N 5.67; S 13.81. $C_{23}H_{23}O_4N_2S_2Cl$. Computed %: N 5.71; S 13.84.

SUMMARY

The synthesis of 9 cyanin dyes of a new group – the benzo-1,4-thiazinecyanins – has been described, namely; two monomethyne-, six trimethyne- and one pentamethynecyanin. It has been shown that when quaternary salts of benzo-1,4-thiazine and of its derivatives are heated with the ester of orthoformic acid in pyridine or in a pyridine-acetic anhydride mixture, isomerization results in the simultaneous formation of thiacarbocyanins and thiazinocarbocyanins.

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*See CB translation p. 169 ff.

**See CB translation p. 185 ff.

***See CB translation p. 543 ff.

RESEARCHES ON THE DERIVATIVES OF BENZO-1,4-THIAZINE

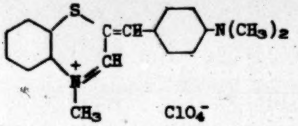
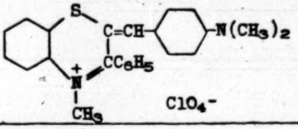
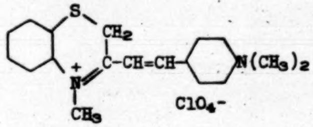
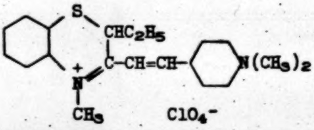
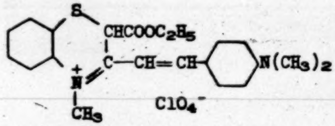
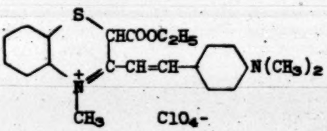
III. CONDENSATION OF QUATERNARY SALTS OF BENZO-1,4-THIAZINE AND OF ITS DERIVATIVES WITH ALDEHYDES

A. I. Kiprianov and Z. N. Pazenko

When the quaternary salts of 3-methylbenzo-1,4-thiazine and its derivatives [1] are heated in acetic anhydride, they condense readily with p-dimethylaminobenzaldehyde. This produced high yields of styryls, the red or purple solutions of which are able to change their color to yellow when even weak solutions of alkali, such as ammonia or pyridine, are added, and in some cases, even when plain water is added. When these yellow solutions are acidulated with a mineral acid, the original color is restored to its initial intensity before alkalinization.

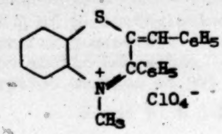
The methyl perchlorates of benzo-1,4-thiazine and 3-phenylbenzo-1,4-thiazine, which do not contain a reactive methyl group at the 3-position, enter into condensation reactions with p-dimethylaminobenzaldehyde nonetheless, giving rise to deeply colored products. The ability of these compounds to condense with the aldehydes might be explained as due to their isomerization to quaternary salts of benzothiazole, but then we should recover the well-known styryls. Comparison of the absorption curves and maxima of the compounds synthesized with the absorption curves of the styryls of the corresponding derivatives of benzothiazole indicates, however, that the coloration of the latter is much higher than that of the preparations we have synthesized. When the methyl perchlorate of benzo-1,4-thiazine was condensed with p-dimethylaminobenzaldehyde, we secured a product with an absorption maximum at 585 mμ, whereas the corresponding product in the benzothiazole series [the methyl perchlorate of 2-(p-dimethylaminostyryl)-benzothiazole] has an absorption maximum at 530 mμ [2]. The condensation product of the methyl perchlorate of 3-phenylbenzo-1,4-thiazine has an absorption maximum at 605 mμ, whereas the corresponding styryl of the benzothiazole series [the methyl perchlorate of β-phenyl-2-(p-dimethylaminostyryl)-benzothiazole] has an absorption maximum at 510 mμ [3]. The fact that these new preparations are extremely unstable in the presence of alkalies is further proof that they belong to the benzo-1,4-thiazine rather than the benzothiazole series.

Thus, the condensation of the quaternary salts of the derivatives of benzo-1,4-thiazine with p-dimethylaminobenzaldehyde does not involve the isomerization of the ring. Apparently, these salts, which have no reactive methyl group, condense at the

Name of the quaternary salt	Formula of the synthesized styryl and its absorption maximum	
Methyl perchlorate of benzothiazine	(I) 	585 mμ
Methyl perchlorate of 3-phenylbenzothiazine	(II) 	605 mμ
Methyl perchlorate of 3-methylbenzothiazine	(III) 	572 mμ
Methyl perchlorate of 2-ethyl-3-methylbenzothiazine	(IV) 	560 mμ
Methyl perchlorate of 2-carbethoxy-3-methylbenzothiazine	(V) 	565 mμ
Phenyl perchlorate of 2-carbethoxy-3-methylbenzothiazine	(VI) 	571 mμ

methylene group at the 2-position in the thiazine ring. The formulas of the preparations we have synthesized are listed in the table, together with their absorption maxima.

p-Dimethylaminobenzaldehyde may condense with the methyl perchlorate of 3-methylbenzothiazine either at the methylene group in the 2-position or at the methyl group in the 3-position. That is why the structure (III), which we have adopted for this preparation on the basis of the closeness of its absorption maximum to that of the preparations (IV-VI), cannot be accepted as definitely established.



(VII)

In order to prove the reactivity of the methylene group in the 2-position of the 1,4-thiazine ring, we condensed the methyl perchlorate of 2-phenylbenzo-1,4-thiazine with benzaldehyde and obtained a product that proved upon analysis to be the methyl perchlorate of 2-(p-dimethylaminobenzylidene)-3-phenylbenzothiazine (VII).

EXPERIMENTAL

Methyl perchlorate of 2-(p-dimethylaminobenzylidene)-benzo-1,4-thiazine (I). 0.2 g of the methyl perchlorate of benzo-1,4-thiazine and 0.12 g of p-dimethylaminobenzaldehyde were heated to boiling in 1 ml of acetic acid for 1 minute. The mixture turned an intense blue, but the color disappeared with further boiling. The dye was immediately precipitated with ether, washed repeatedly with ether on the filter, and precipitated with ether from acetic anhydride. Yield 0.08 g; blue needles with a temp. decomp. of 135-137°. Absorption maximum in acetic acid 585 mμ. Alcoholic solutions are hydrolyzed upon standing.

Found %: N 6.85. $C_{18}H_{19}O_4N_2SCl$. Computed %: N 7.10.

When the foregoing condensation is performed in acetic anhydride to which a few drops of pyridine have been added, a pink solution of the perchlorate of 2-(p-dimethylaminostyryl)-benzothiazole results, with an absorption maximum at 530 mμ.

Methyl perchlorate of 2-(p-dimethylaminobenzylidene)-3-phenylbenzo-1,4-thiazine (II). A solution containing 0.2 g of the methyl perchlorate of 3-phenylbenzothiazine and 0.09 g of p-dimethylaminobenzaldehyde in 3 ml of acetic anhydride was boiled for 5 minutes, and then the dye was precipitated from the cooled solution with ether and recrystallized twice from alcohol. Yield 0.17 g, or 67% of the theoretical. Blue needles with a silvery luster; absorption maximum in an alcoholic solution at 605 mμ.

Found %: N 5.48; S 6.21. $C_{24}H_{23}O_4N_2SCl \cdot 3H_2O$. Computed %: N 5.56; S 6.33.

Methyl perchlorate of 3-(p-dimethylaminostyryl)-benzothiazine (III). 0.5 g of the methyl perchlorate of 3-methylbenzothiazine and 0.27 g of p-dimethylaminobenzaldehyde were heated for 5 minutes in 5 ml of acetic anhydride. The precipitate that was thrown down upon cooling was recrystallized twice from alcohol. Purple crystals with a coppery sheen. Temp. decomp. 162-166°; absorption maximum at 572 mμ. Yield 0.19 g, or 24% of the theoretical.

Found %: N 6.72; Cl 8.62; S 7.83. $C_{19}H_{21}O_4N_2SCl$. Computed %: N 6.86; Cl 8.69; S 7.85.

Methyl perchlorate of 2-ethyl-3-(p-dimethylaminostyryl)-benzo-1,4-thiazine (IV). 0.3 g of the methyl perchlorate of 2-ethyl-3-methylbenzothiazine and 0.15 g of p-dimethylaminobenzaldehyde in 2 ml of acetic anhydride were boiled for 10 minutes. After part of the acetic anhydride had been driven off in vacuum, the styryl was recovered as an amorphous golden-colored mass. After recrystallization from alcohol, the preparation consisted of lustrous greenish platelets with an absorption maximum in alcoholic solution at 560 mμ. Yield 0.1 g, or 23% of the theoretical.

Found %: N 6.18. $C_{21}H_{25}O_4N_2SCl$. Computed %: N 6.42.

Methyl perchlorate of 2-carbethoxy-3-(p-dimethylaminostyryl)-benzo-1,4-thiazine (V). 0.5 g of the methyl perchlorate of 2-carbethoxy-3-methylbenzo-1,4-thiazine, 0.2 g of p-dimethylaminobenzaldehyde, and 3 ml of acetic anhydride were boiled together for 5 minutes. The dye that precipitated out after cooling was recrystallized from acetic anhydride. Yield: 52% of the theoretical. Golden-purple crystals. Absorption maximum at 565 mμ.

Found %: N 5.62: $C_{22}H_{25}O_8N_2S_2Cl$. Computed %: N 5.83.

Phenyl perchlorate of 2-carbethoxy-3-(p-dimethylaminostyryl)-benzo-1,4-thiazine (VI). 0.5 g of the phenyl perchlorate of 2-carbethoxy-3-methylbenzothiazine and 0.18 g of p-dimethylaminobenzaldehyde were boiled for 10 minutes with 3 ml of acetic anhydride. The tarry product that settled out was washed with benzene and recrystallized from absolute alcohol. Golden-green platelets. Yield 35% of the theoretical; absorption maximum at 571 mμ.

Found %: N 5.29. $C_{27}H_{27}O_6N_2SCl$. Computed %: N 5.45.

Methyl perchlorate of 2-benzylidene-3-phenylbenzo-1,4-thiazine (VII). 0.2 g of the methyl perchlorate of 3-phenylbenzothiazine and 0.3 g of benzaldehyde were heated to 100° for 1 hour in a sealed tube. The condensation product was washed with ether and recrystallized twice from absolute alcohol. This yielded 0.12 g (48% of the theoretical) of a brown crystalline product.

Found %: N 3.19; S 7.11. $C_{22}H_{18}O_4NSCl$. Computed %: N 3.27; S 7.48.

SUMMARY

It has been shown that when the quaternary salts of 3-methylbenzo-1,4-thiazine and of some of its derivatives are condensed with p-dimethylaminobenzaldehyde in acetic anhydride, the corresponding styryls are formed, which are not proof against the action of alkalies. The quaternary salts of benzo-1,4-thiazine and its derivatives, which have no methyl group at the 3 position, condense at the methylene group in the 2 position of the thiazine ring with aromatic aldehydes.

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[*] See CB translation p. 169 ff.

[**] See CB translation p. 543 ff.

THE ALKALOIDS OF *DELPHINIUM SEMIBARBATUM*. II

IV ALKALOIDS OF THE *RANUNCULACEAE* FAMILY

S Yunusov and N. K. Abubakirov

Delphinium semibarbatum Bienert (local name: "isparyak") is widely distributed over almost all the territory of Central Asia. The local population makes a bright-yellow dye "zalil" from its flowers, which is used to dye wool, silk, and cotton fabrics. The coloring matter in the flowers has been investigated chemically [1]; it is a mixture of quercetin $C_{15}H_{10}O_7$ and isoremnetin $C_{16}H_{12}O_7$. It has been recently found that the vegetable dye is suitable for coloring photographic and optical light filters [2]. No detailed research has been done on the plant's alkaloids.

Pursuing our research on the aconitic and delphinic alkaloids [3], we resolved to study the chemical nature of the alkaloids contained in *D. semibarbatum*. In connection with the research being conducted in our laboratory on the role of alkaloids and the dynamics of their accumulation [4], we were likewise interested in how the alkaloids were localized during the various growth periods of the plant. We found that the part of the plant above ground (leaves and stems) contains a maximum quantity of alkaloids (0.25%) during the initial growth period, before flowering. During the flowering period the percentage of alkaloids drops sharply (0.09%) in the above-ground parts of the plant, falling to 0.07% during the fruit-bearing period. This is paralleled by an accumulation of the alkaloids in the seeds (0.56%). A slight change in the percentage of alkaloids likewise takes place in the roots (0.11% before flowering and 0.13% during the fruit-bearing period).

This is further confirmation of the behavior pattern that we have repeatedly observed in other plants: quantitative (and sometimes qualitative) changes in the alkaloids in the different organs of the plant continue throughout the entire vegetation period, the percentage of alkaloids being a maximum in the organs that are the "principal" ones at the given time. The green parts of the plant are such organs during the period of growth, while after the growing season these organs are the seeds and the roots, where the plant "stores up" the substances necessary for its activity. Qualitatively, the same alkaloids are found throughout the period of development.

The alkaloid *delsemin*, discovered by us, constitutes the bulk of the mixture of bases recovered by the usual dichloroethane extraction. Though the base is at once recovered in crystalline form, it retains its brown coloring so tenaciously that its refining demands considerable effort. The alkaloid can be crystallized only from acetone or alcohol diluted with water. The base is precipitated from other solvents for the most part as a thick amorphous mass. Delsemin crystallizes with a varying amount of water, which is hard to determine. Its form in which it contains half a molecule of water appears to be the most stable one. The data of the analysis of this compound indicate a formula of $C_{37}H_{53}O_{10}\cdot\frac{1}{2}H_2O$. Any effort to drive out all the water of crystallization by desiccation in vacuum results in the disintegration of the alkaloid. The salts of delsemin are hygroscopic, deliquescing quickly in the air, and we were therefore unable to obtain them in the crystalline form under ordinary conditions.

Delsemin is extremely unstable in the presence of alkalies or acids, even very weak ones. Even brief storage of aqueous solutions of its salts results in the hydrolytic decomposition of the base. In determining the esterified acids in the alkaloid by saponification, we use a quantity of the alkali that corresponds approximately to the presence of two acid groups. Ordinary saponification with a 10% solution of caustic potash, however, resulted in the isolation of only one acid – anthranilic acid. Investigation of the conditions and rate of saponification of delsemin has shown that heating the alkaloid for a very short time with an exactly equivalent quantity of a 1N alkali yields a wholly different monobasic acid, hitherto unknown, which we have named delseminic acid. As our observations have shown, the excess of alkali over the equivalent quantity is consumed in the further saponification of the delseminic acid. The readiness with which delsemin is hydrolyzed leads us to suppose that its esterified hydroxyl group must be either a primary or a secondary one.

The elementary analysis of delseminic acid agrees with the formula $C_{12}H_{14}O_4N_2$, even though only a small quantity of the acid has been synthesized. Solutions of the acid rotate the plane of polarization to the left. Research on the structure of the acid is now under way.

Another product of the saponification of delsemin is an alkamine – delsin. We discovered the latter in the plant and in the free, unesterified state. It is quite possible that it is merely the product of the decomposition of delsemin when the latter is isolated from the vegetable raw material, but delsin has been invariably found under the most varied conditions, as one of the constituents of the alkaloid mixture, in all of our extractions. Delsin crystallizes from dilute alcohol with one molecule of water of crystallization, which it retains tenaciously. When the water of crystallization is driven off by drying in vacuum at 100-105°, the base loses its crystalline structure, turning into an amorphous hyaline mass. In air, however, the alkaloid absorbs water and slowly changes back into the crystal hydrate. In contrast to delsemin, delsin yields a number of well-crystallized salts: the hydrochloride, the hydrobromide, the hydriodide, the perchlorate, and the crystalline iodomethylate.

The elementary analysis of the base and of its salts indicate that its empirical formula is $C_{25}H_{41}O_7N\cdot H_2O$. The functions of the oxygen atoms are distributed as follows: 3 belong to hydroxyl groups, and 4 to methoxy groups. Delsin was oxidized with potassium permanganate in order to determine the nature of the alkyl imide groups in that alkaloid. We succeeded in recovering acetaldehyde; this was proved by synthesizing the latter's condensation product with dinitrophenylhydrazine. Thus, the formula of delsin may be partially depicted as follows, on the basis of our determination of the nature of its functional groups:

$$C_{25}H_{41}O_7N = C_{19}H_{21}(NC_2H_5)(OH)_3(OCH_3)_4.$$

The formula for delsemin, however, looks like this:

$$C_{37}H_{53}O_{10}N_3 = C_{19}H_{21}(NC_2H_5)(OH)_2(OCH_3)_4(OCOC_{11}H_{14}O_2N_2).$$

This is not the first time that bases which are esterified by derivatives of anthranilic acid have been discovered among the aconitic and delphinic alkaloids.

In 1913, Schulze and Bierling made a study of the roots of *Aconitum lycoctonum* and isolated the amorphous alkaloid *lycaconitine*, which upon hydrolysis yielded succinylanthranilic acid and the amino alcohol lycoctonine. Many years later, Goodson [6] saponified the alkaloids methyllycaconitine and ajacine, isolated from *D. elatum* and *D. ajacis*, respectively, together with methylsuccinylanthranilic and acetylanthranilic acids, and recovered the very same amino alcohol, which the author took to be lycoctonine because of the similarity of certain of their properties. Marion and Manske [7] hydrolyzed an alkaloid they had isolated from *D.Brownii* and secured methylsuccinylanthranilic acid plus the same lycoctonine, which they identified with a genuine sample of lycoctonine specially isolated for the purpose from *A.Lycoctonum*. Subsequently, one of these authors [8] discovered lycoctonine in the alkaloids of *D. consolida* as well.

As the foregoing survey of the literature indicates, lycoctonine, which is esterified by one derivative or another of anthranilic acid, is an alkaloid that is common to several *Delphiniums*. And inasmuch as our amino alcohol delsin was also no doubt found in a compound with a derivative of anthranilic acid and possessed several properties that resembled those of lycoctonine, we decided to compare some of the figures for the two alkaloids (*cf* the Table).

Constants	Delsin	Lycoctonine		
	Our data	Schulze and Bierling	Goodson	Marion and Manske
Formula	$C_{25}H_{41}O_7N \cdot H_2O$	$C_{25}H_{39}O_7N \cdot H_2O$		$C_{20}H_{33}NO_5 \cdot H_2O$
Function groups	3 OH, 4 OCH_3	2 OH, 4 OCH_3	3 OH, 4 OCH_3	3 OCH_3
Melting point	140°*	131-133°***	141°*	139°*
$[\alpha]_D$ in alcohol	+51.74°	+49.64°	+ 53.20°	+ 52.20°
M.p. of hydrochloride	165°	75°***	–	145°
M.p. of hydrobromide	185°	88-89°	–	above 360°
M.p. of perchlorate	145-146°	68-69°	–	215°
M.p. of iodomethylate	189-190°	178°	–	187°

The table indicates that although the melting points and the specific rotatory power of delsin and lycoctonine are quite comparable, and the molecular formulas and the substituting groups are likewise comparable in the first three columns, the melting points of the salts of our alkaloid differ markedly from the corresponding figures for lycoctonine. We therefore believe that delsin is a new alkaloid, not described in the literature, which may be an isomer of lycoctonine.

In conclusion, we wish to express our gratitude to the co-workers of our laboratory, R.I.Milkovskaya and D.M.Gusevaya, who carried out the bulk of the analytical determinations.

EXPERIMENTAL

The quantitative determination of the alkaloids during the various growth periods was done in an extractor specially designed in our laboratory for this purpose; it has the advantage over the usual extractors of the Soxhlet type that it enables one to take continuous micelle samplings throughout the alkaloid extraction process. 400-450 g of the plant are wetted down with a 10-12% ammonia solution, charged into this apparatus and continuously extracted with ether. The completeness of extraction is determined by reacting a sample with silicotungstic acid. The ether extract is evaporated and agitated with the acid. Subsequently, the total alkaloids are determined in the usual manner.

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*All Melting points are corrected.

**Uncorrected melting points.

***Salts were not recrystallized or desiccated.

Isolation and separation of the total alkaloids. 22.5 g of the dry and pulverized plant (above ground parts*) are wetted with 16 liters of a 5% ammonia solution and charged into a percolator, into which 110 kg of dichloroethane is poured 3 hours later. Extraction is effected in the cold, in a room whose temperature is kept at 3-5°. Daily, for a week, the dichloroethane extract is decanted and agitated with a sulfuric acid solution, a 10% solution the first time, and a 5% solution the next two times. The acid solutions are combined, filtered, and alkalinized in the cold with a 25% ammonia solution, an effort being made to avoid using an excess if possible. The precipitate that is thrown down is suction filtered, washed with water, and then washed on the filter while wet with alcohol or acetone. After the alcohol has been evaporated in pans in the open air, the residue solidifies as a dense crystalline mass of delsemin. Weight after drying in a vacuum exsiccator over H_2SO_4: 18 g.

After the delsemin had been removed, the brown aqueous mother liquor, totaling 6 liters, was extracted 3 times with 300 ml of ether (Solution A). Then the mother liquor was mixed with 1 liter of 50% KOH, chilled, and again extracted with ether (Solution B). Finally, the alkaline solution was exhaustively extracted with chloroform.

After the ether had been driven off from Solution A, there was left 1.3 g of a transparent hyaline mass, which was a mixture of delsemin and delsin. The latter was saponified by a method described later, yielding 0.9 g of delsin and 0.2 g of anthranilic acid. After evaporation, Solution B yielded 0.9 g of nearly pure delsin. The chloroform portion of the alkaloid mixture, totaling 1.0 g, was not analyzed further for the time being. The total alkaloid yield was 20.2 g, or 0,09% of the dry plant weight. 13.8 g of total alkaloids (0.12%) was extracted from 11.5 kg of the roots by the method described above.

Purifying delsemin. 18.0 g of the commercial base was continuously extracted with separate batches of anhydrous ether until the bulk of the delsemin had entered solution. The ether was driven off, and the residue, a dark-yellow, viscous mass, was dissolved in 28 ml of 1 N hydrochloric acid. The acid solution was extracted with chloroform and fractionally alkalinized with 1 N caustic potash. Each time 4 ml of the alkali was added, and the base that precipitated out was extracted with an equal volume of ether. After 12 ml of caustic potash had been added, the time came when the precipitate thrown down by the addition of the next batch of alkali filled the whole solution, and the base transferred to the ether was immediately reprecipitated as fine crystals. We then ceased further fractionation, and the jellylike mass was poured off and alkalinized with a slight excess of ammonia. The precipitated delsemin, which was still colored, was washed with water and recrystallized from 25 ml of a 30% aqueous solution of alcohol. This recrystallization was repeated three times, the alcohol concentration being gradually raised to 60-65%. The solution was heated with activated charcoal prior to the last recrystallization. The delsin crystals became pure white after this refining process. Neither the melting point nor the specific rotatory power was changed by further recrystallization. Yield 6.4 g.

Delsemin

Delsemin crystallizes from dilute alcohol as very thin silky fibers, diverging from a single center. The fibers conglomerate when filtered, turning into a clotted mass, which is hard to suction-filter. To remove the last traces of the solvent, the product was set aside overnight above calcium chloride in a vacuum exsiccator. The freshly recrystallized base, desiccated as set forth above, collects as much as four molecules of water in a few days when exposed to the air.

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*The plants used in this research were gathered toward the end of May 1946, during the period of full full flowering, on the wooded hills in the Akhan Garan District of Tashkent Region.

> 0.5034 g substance: 0.0460 g H_2O (at 105-110° and 5 mm). Found %: H_2O 9.14. $C_{37}H_{53}O_{10}N_3 \cdot 4H_2O$. Computed %: 4 H_2O 9.34.

The tetrahydrate form of delsemin is apparently unstable, since the crystals begin to dry out when kept for a long time, gradually turning into a form that corresponds approximately to two molecules of crystallization water. This causes the alkaloid to darken slowly.

> 1.0766 g substance: 0.0568 g H_2O (at 100-105° and 7 mm). 0.4560 g substance: 0.0252 g H_2O (at 100-105° and 9 mm). Found %: H_2O 5.28, 5.53. $C_{37}H_{53}O_{10}N_3 \cdot 2H_2O$. Computed %: $2H_2O$ 4.90.

The base is converted into a form containing half a molecule of water when dried in vacuum at 70-80° or when kept in an exsiccator for an extremely long time. This last form is very stable. When an endeavor is made to eliminate the water by raising the temperature to 100-105°, the delsemin decomposes, turning yellow. The physical constants were determined and the analysis made with this form.

Delsemin does not have a sharp melting point. It begins to soften at 119°, becoming transparent at 121°, and fusing at 125° with foaming. The alkaloid is highly soluble in chloroform, methanol, and ethyl alcohol (1:2), acetone, and benzene; it dissolves in the proportions of 1:75 in anhydrous ether, is soluble with difficulty in water (1:800), and is practically insoluble in petroleum ether.

> 0.5050 g substance dissolved in 25.0 ml of alcohol; $\underline{l}$ = 10.0; α_D = = +0.87°, $[\alpha]_D^{14} = +43.07°$. 0.1142 g substance: 0.2610 g CO_2; 0.0796 g H_2O. 0.1104 g substance: 0.2528 g CO_2; 0.0790 g H_2O. 0.1440 g substance: 0.3296 g CO_2; 0.1024 g H_2O. 0.1664 g substance: 9.33 ml N_2 (27°, 720 mm). 0.1750 g substance: 9.80 ml N_2 (27°, 719 mm). 0.0222 g substance: 7.30 ml 0.1 $\underline{N}$ $Na_2S_2O_3$ (Wibock). 0.0272 g substance: 8.90 ml 0.1 $\underline{N}$ $Na_2S_2O_3$. 0.1508 g substance: 4.30 ml 0.05 $\underline{N}$ HCl (potentiometry). Found %: C 62.37, 62.49, 62.46; H 7.80, 8.00, 7.96. N 5.82, 5.81; OCH_3 17.00, 16.92. Equiv. 701.4. $C_{37}H_{53}O_{10}N_3 \cdot \frac{1}{2}H_2O$. Computed %: C 62.69; H 7.68; N 5.93; $4OCH_3$ 17.51; equiv. 708.8.

Saponification of delsemin. Experiment 1. 0.5160 g of the base was heated with 30 ml of alcohol and 29 ml of 0.1 $\underline{N}$ KOH over a water bath with a reflux condenser. To protect the mixture against the effect of carbon dioxide, a tube containing soda lime was attached to the open end of the condenser. Three hours later the alcohol was driven off, and the resulting amino alcohol was extracted with ether. Extraction was continued until the last batch of ether gave a negative reaction for the presence of alkaloids. The combined ether solution was agitated three times with small batches (10 ml) of water which was then added to the initial alkaline solution. The excess of unreacted alkali was titrated back against phenolphthalein with 0.1 $\underline{N}$ H_2SO_4. Found: 13.8 ml. The computed value for two equivalents is 14.6 ml of 0.1 $\underline{N}$ KOH.

Experiment 2. 1.60 g of delsemin was dissolved in 15 ml of methanol, 1.5 g of KOH was added, and the whole was boiled for 2 hours over a water bath. Toward the end of the test the methanol was driven off, after which the mixture was evaporated to dryness in vacuum. The residue was diluted with 15 ml of water and left to stand overnight. The next day the crystals that had settled out were separated and washed 2 to 3 times with small batches of water. The crystals fused at 137-138° after recrystallization from 65% alcohol. They exhibited no depression in a mixed test sample. The alkaline mother liquor was repeatedly extracted with chloroform, a small quantity of delsin being recovered after the chloroform had been driven off. Total yield of the alkamine: 0.93 g.

The solution, separated from the chloroform, was diluted to a volume of 30 ml and acidulated with 10% H_2SO_4 until its reaction was neutral. The tar that settled was filtered out, and the filtrate was reacuidulated and set aside for 2 days. Oil settled out again, gradually turning into a dense crystalline mass. Yield 0.21 g. The crystals had a m.p. of 146° after double recrystallization from hot water. A test sample mixed with anthranilic acid, fused at 146-147°.

> 0.0714 g substance: 0.1596 g CO_2; 0.0350 g H_2O. 0.0790 g substance: 7.85 ml N_2 (28°, 714 mm). 0.0308 g substance: 2.18 ml 0.1 N KOH (phenolphthalein). Found %: C 61.00; H 5.49; N 10.16; equiv. 141.3. $C_7H_7O_2N$. Computed %: C 61.30; H 5.15; N 10.21; equiv. 137.1.

The anthranilic acid mother liquor was repeatedly extracted with ether. After the ether had been driven off, a small quantity of tar was left, which we were unable to crystallize.

Experiment 3. 5.5 ml of 1.162 N KOH was added to a hot solution of 4.50 g of delsemin in 40 ml of methanol, and the alcohol was driven off as rapidly as possible (within 15-20 minutes). After most of the solution had evaporated, the residue was chilled, and caused to crystallize by shaking. The delsin that settled out was suction filtered and washed with a few milliliters of water. The wash waters were combined with the alkaline mother liquor, and the latter was extracted 5 times with ether. The chloroform and ether solutions were washed twice with 2-3 ml of water, which was then added to the same alkaline solution. After the chloroform and the ether had been driven off, 0.45 g of delsin was left. The total yield of the alkamine was 2.95 g, or 96% of the computed value.

After all the amino alcohol had been extracted, the aqueous solution was fractionally acidulated with 6.2 ml of 1.0245 N sulfuric acid, at the same time being extracted with equal volumes of ether. The first fraction, taken after 1.0 ml of H_2SO_4 had been added, was highly fluorescent; after the ether had been driven off, a minute quantity of anthranilic acid was left. The fluorescence disappeared when the subsequent batches of acid were added, and crystals that were insoluble in water or in ether began to settle out. Then extraction with ether was stopped, and the aqueous solution was gradually acidulated further with the remaining acid until all the latter had been used up. The 1.20 g of delseminic acid that settled out had a m.p. of 168-170° (shrank at 166°).

The delseminic acid mother liquor was repeatedly extracted with ether, another 0.29 g of the acid being recovered after the ether had been driven off. Total yield of the acid: 1.49 g. Expected yield: 1.59 g.

Delseminic Acid

When recrystallized from an alcohol-ether mixture, the acid settles out as colorless crystals, gathered into large warty nodules, with a m.p. of 170-171° (shrinks at 168°). It contains no crystallization solvent. The optical activity of the acid disappears when aqueous solutions are heated for a long time, and then it fuses at 180-181°. Delseminic acid is readily soluble in alcohol (1:6), but soluble with difficulty in ether (1:330) and in water (1:400).

> 0.6516 g substance in 10.5 ml alcoholic solution: $l = 10.0$; $\alpha_D = -0.04°$, $[\alpha]_D^{15} = -0.64°$. 0.0922 g substance: 0.1942 g CO_2;

0.0492 g H_2O. 0.1150 g substance: 0.2430 g CO_2; 0.0600 g H_2O. 0.0776 g substance: 8.40 ml N_2 (29.5°, 716 mm). 0.1152 g substance: 11.38 ml N_2 (18°, 733 mm). 0.0744 g substance: 2.97 ml 0.1 N KOH (phenolphthalein). Found %: C 57.48, 57.66; H 5.97, 5.84. N 11.02, 10.95; equiv. 250.0. $C_{12}H_{14}O_4N_2$. Computed %: C 57.59; H 5.64; N 11.19; equiv. 250.4.

Delsin

Purification. 6.0 g of commercial delsin was suspended in 12 ml of methanol, and dissolved by the addition of 2-3 ml of concentrated hydrobromic acid until its reaction to Congo was slightly acid. 18 ml of ether was added from the top, along the walls of the vessel. After some time had elasped, beautiful, rapidly growing crystals of delsin hydrobromide began to settle out at the boundary between the two layers. The resulting salt was recrystallized from methanol diluted with ether, and then dissolved in 30 ml of water. The base is precipitated from the hydrobromide by alkalinizing the solution with concentrated ammonia. The finely crystalline base that was secured was suction-filtered and recrystallized from 15 ml of 70% alcohol.

Properties. The base crystallizes in perfectly regular orthogonal prisms with one molecule of water. The alkaloid produced via the hydrobromide shrinks at 136° and fuses with foaming at 140° (a capillary was inserted at 130°). When purified via another salt, the base has the same melting point. Delsin is a rather strong base; its solutions change the color of phenolphthalein as well as of litmus. Delsin is highly soluble in chloroform, somewhat less so in alcohol (1:8) and acetone, soluble with difficulty in water (1:130) and ether (1:275), and nearly insoluble in petroleum ether. The whole analysis was effected with the monohydrate form of the alkaloid.

0.5218 g substance in 25 ml absolute alcohol solution: l = 10.0; $\alpha_D = +1.08°$; $[\alpha]_D^{15} + 51.74°$. 0.1380 g substance: 0.3114 g CO_2; 0.1134 g H_2O. 0.1014 g substance: 0.2292 g CO_2; 0.0826 g H_2O. 0.1146 g substance: 3.18 ml N_2 (24°, 721 mm). 0.1442 g substance: 4.05 ml N_2 (30°, 716 mm). 0.1111 g substance: 19.84 ml CH_4 (0°, 760 mm) (Terevitinov). 0.1225 g substance: 21.66 ml CH_4 (0°, 750 mm). 0.0262 g substance: 12.80 ml 0.1 N $Na_2S_2O_3$ (Wibock). 0.0254 g substance: 12.40 ml 0.1 N $Na_2S_2O_3$. 0.1080 g substance: 22.33 ml 0.01 N HCl. (Potentiometry). 0.1344 g substance: 27.70 ml 0.01 N HCl. Found %: C 61.58, 61.68; H 9.19, 9.11; N 2.93, 2.85; OH 13.64, 13.51; OCH_3 25.26, 25.24; equiv. 483.7, 485.2. $C_{25}H_{41}O_7N \cdot H_2O$. Computed %: C 61.83; H 8.93; N 2.88; 4OH 14.01; $4OCH_3$ 25.56; equiv. 485.6.

The only way to get rid of the molecule of water of crystallization in delsin is by desiccating the base at 100-105°. This causes the alkaloid to lose its crystalline structure, however, deliquescing into an amorphous mass. Anhydrous delsin shrinks at 120°, becomes transparent at 125°, and foams at 138°. Goodson made the same observations upon lycoctonine [6]. In general, it must be said that Goodson's lycoctonine's properties are very close to those of our delsin, which cannot be said of the lycoctonine isolated by Marion and Manske [7].

0.1202 g substance: 0.0044 g H_2O (at 100-105° and 16 mm). 0.1802 g substance: 0.0068 g H_2O (at 100-105° and 18 mm). Found %: H_2O 3.66, 3.77. $C_{25}H_{41}O_7N \cdot H_2O$. Computed %: H_2O 3.71. 0.1158 g substance: 0.2716 g CO_2; 0.0930 g H_2O. 0.0986 g substance: 0.2308 g CO_2; 0.0800 g H_2O. Found %: C 64.00, 63.88; H 8.99, 9.08. $C_{25}H_{41}O_7N$. Computed %: C 64.24; H 8.84.

Salts of delsin. Hydrochloride. 0.52 g of the base was mixed with an equivalent quantity of an alcoholic solution and placed in an exsiccator above sulfuric acid for 1-2 days until all the alcohol had evaporated. The lusterless crust that formed turned into a white crystalline powder when pulverized. After being recrystallized from a mixture of 2 ml of anhydrous alcohol and 4 ml of ether, the delsin hydrochloride settled out as large orthogonal prisms, resembling minature railway ties. The salt apparently crystallizes with a fractional number of molecules of crystallization water.

> 0.2986 g substance: 0.0064 g H_2O (at 100-110° and 7 mm). 0.1936 g substance: 0.0046 g H_2O (at 100-105° and 12 mm). Found %: H_2O 2.14, 2.38. $C_{25}H_{41}O_7N \cdot HCl \cdot H_2O$. Computed %: H_2O 3.45. $C_{25}H_{41}O_7N \cdot HCl \cdot \frac{2}{3}H_2O$. Computed %: H_2O 2.33.

When exposed to air, the hydrochloride absorbs moisture rapidly and deliquesces. Alcoholic solutions of the salt exhibit violet fluorescence. Delsin hydrochloride is readily soluble in alcohol and acetone as well as in water. The salt was analyzed after having been desiccated in vacuum; it had a m.p. of 165° (with decomp.).

> 0.2276 g substance, in 10.5 ml water: $\underline{l} = 10.0$; $\alpha_D = +0.30°$; $[\alpha]_D^{15} = +13.84°$; 0.0240 g substance: 0.92 ml 0.05 $\underline{N}$ $AgNO_3$. 0.0402 g substance: 1.53 ml 0.05 $\underline{N}$ $AgNO_3$. Found %: Cl 6.80, 6.75. $C_{25}H_{41}O_7N \cdot HCl$. Computed %: Cl 7.03.

Hydrobromide. Delsin hydrobromide is recovered as very large, compact prisms, containing two molecules of water of crystallization, after recrystallization from a methanol-ether mixture.

> 0.3418 g substance: 0.0224 g H_2O (at 100-105° and 20 mm). 0.3408 g substance: 0.0214 g H_2O (at 100-105° and 20 mm). Found %: H_2O 6.55, 6.28. $C_{26}H_{41}O_7N \cdot 2HBr \cdot H_2O$. Computed %: $2H_2O$ 6.16.

When exposed to the air, the salt absorbs up to 4 molecules of water, but it does not lose its crystalline structure, in contradistinction to the hydrochloride. The anhydrous salt fuses at 185° (with decomp).

The hydrobromide of lycoctonine synthesized by Marion and Manske in exactly the same way crystallized with a molecule of methanol and shrank at 225°, turned black at about 260°, and did not fuse even at 360°.

> 0.3000 g substance in 10 ml water; $\underline{l} = 10.0$; $\alpha_D = +0.42°$, $[\alpha]_D^{18} = +14.00°$. 0.1036 g substance: 3.78 ml 0.05 $\underline{N}$ $AgNO_3$ (potentiometry). 0.1742 g substance: 6.28 ml 0.05 $\underline{N}$ $AgNO_3$. Found %: Br 14.58, 14.41. $C_{25}H_{41}O_7N \cdot HBr$. Computed %: Br 14.57.

Hydriodide. 0.5 g of delsin was mixed with 2 ml of alcohol and then acidulated with hydriodic acid until its reaction to Congo was slightly acid. All the base dissolved at first, but after a short time delsin hydriodide began to settle out. After recrystallization from alcohol, the salt forms light-yellow crystals of the monoclinic system, with a m.p. of 173-175°, containing 8-9% of crystal water or alcohol. The desiccated salt shrinks at 184° and fuses at 188-189°. Delsin hydriodide differs from the hydrochloride and the hydrobromide in being soluble with difficulty in alcochol.

> 0.3028 g substance in 25 ml absolute alcohol solution: $\underline{l} = 10.0$; $\alpha_D = +0.38°$, $[\alpha]_D^{15} = +31.37°$. 0.0858 g substance: 2.84 ml 0.05 $\underline{N}$ $AgNO_3$. 0.0962 g substance: 3.18 ml 0.05 $\underline{N}$ $AgNO_3$. Found %: I 21.01, 20.97. $C_{25}H_{41}O_7N \cdot HI$. Computed %: I 21.31.

Perchlorate. 0.4 g of delsin was mixed with 1.5 ml of alcohol, and a few drops of 65% perchloric acid were added to make it dissolve. 4 ml of ether was poured on top of the solution. The next day large crystals of deslin perchlorate began to separate out at the boundary between the two layers. The salt had a m.p. of 145-146° (shrank at 140°) after recrystallization from an alcohol-ether mixture. Repeating the recrystallization did not affect the melting point. Delsin perchlorate is soluble with difficulty in water. It is the only delsin salt that crystallizes without crystal solvent. Alcoholic solutions of the salt exhibit violet fluorescence.

> 0.4762 g substance in 10 ml alcohol: $l = 10.0$; $\alpha_D = +1.19°$, $[\alpha]_D^{15} =$ $= +24.99°$. 0.1342 g substance. 0.0326 g AgCl. 0.1140 g substance: 0.0282 g AgCl. Found %: Cl 6.01, 6.12. $C_{25}H_{41}O_7N \cdot HClO_4$. Computed %: Cl 6.24.

Delsin iodomethylate. 2.26 g of the base and 2.3 ml of methyl iodide were dissolved in 15 ml of methanol and then heated in a sealed tube for 3 hours over a boiling water bath. After the mixture had cooled, the excess methyl iodide and methanol were driven off until the aggregate volume had been reduced to 4-5 ml. An equal quantity of ether was added to the cool solution, instantaneously setting off the crystallization of the delsin iodomethylate. Yield 2.73 g. Expected yield 2.88 g.

When recrystallized from methanol diluted with ether, the iodomethylate settles out as long, regular parallelipipeds, containing 2-2.5% water or methanol of crystallization. The iodomethylate absorbs up to 7% of moisture when exposed to the air. The melting point of the moist iodomethylate is 180-181° (shrinks at 175°), the m.p. being 189-190° (with decomp.) after desiccation in vacuum at 100-105°.

> 0.0566 g substance: 1.84 ml 0.05 N $AgNO_3$. 0.0817 g substance: 2.69 ml 0.05 N $AgNO_3$. 0.0686 g substance: 2.26 ml 0.05 N $AgNO_3$. Found %: I 20.63, 20.89, 20.91. $C_{25}H_{41}O_7N \cdot CH_3I$. Computed %: I 20.82.

Oxidizing Delsin. 0.40 g of potassium permanganate dissolved in 10 ml of water was added during the course of an hour, with constant stirring, to an ice-chilled solution of 1.0 g of the bases in 10 ml of 1 N H_2SO_4. After the solution had been decolorized, the precipitated manganese dioxide was filtered out, and the filtrate was distilled into a well-chilled receiver. 10 ml of a saturated solution of 2,4-dinitrophenylhydrazine in alcohol, containing 1% hydrogen chloride, was added to the resulting distillate, and the mixture was heated over a boiling water bath for a few minutes. Several hours after the mixture had cooled the voluminous precipitate crystallized. Yield 0.11 g. The crystals were separated out, washed with a small quantity of alcohol, and recrystallized from absolute alcohol. The resulting dinitrophenylhydrazone had a m.p. of 166-167°. A test sample, mixed with the condensation product of acetaldehyde and 2,4-dinitrophenylhydrazine, which had a m.p. of 168°, fused at 167-168°.

SUMMARY

1. Two new crystalline alkaloids: delsemin $C_{37}H_{53}O_{10}N_3$, and delsin $C_{25}H_{41}O_7N$, have been isolated from Delphinium semibarbatum (fam. Ranunculaceae) and identified.

2. When saponified with an alkali, delsemin is cleaved into the amino alcohol delsin and an optically active, monobasic amino acid $C_{12}H_{14}O_4N_2$, which we have named delseminic acid.

3. The following partially expanded formulas are suggested for delsemin:

$$C_{19}H_{21}(NC_2H_5)(OH)_2(OCH_3)_4(OCOC_{11}H_{14}O_2N_2),$$

and for delsin:

$$C_{10}H_{21}(NC_2H_5)(OH)_3(OCH_3)_4,$$

on the basis of a quantitative determination of their functional groups.

4. The properties of the alkalmine delsin resemble those of lycoctonine, an alkaloid isolated from *Aconitum lycoctonum*, of which delsin may be an isomer.

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*See CB translation p. 855 ff.

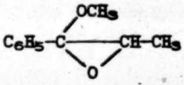
RESEARCHES ON THE CYCLIC ACETALS OF HYDROXY CARBONYL COMPOUNDS

II. THE ACTION OF AN ALKALI UPON 1-METHOXY-1-PHENYLPROPENE-1 OXIDE

T. I Temnikova and E. N. Kropacheva

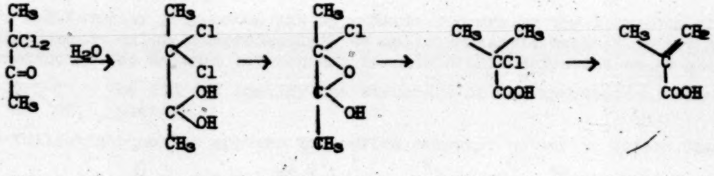
In our previous paper [2] we synthesized an extremely unstable substance, an ether of an α-alcohol oxide- 1-methoxy-1-phenylpropene-1 oxide – for the first time

We were interested in exploring the transformation of this compound in an alkaline medium, since the literature refers to conjectures concerning the formation of substances of this type as intermediate products during the synthesis of unsaturated and saturated acids from the α-halogen ketones.



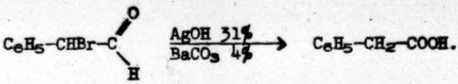
(I)

The acid conversion of the α-halogen ketones when reacted with alkalies was discovered by A.E.Favorsky in the transformation of α-dichloro ketones into acrylic acids [2]. To explain the mechanism of these transformations, A.E.Favorsky advanced the hypothesis that hydrates were first formed by the addition of water to the carbonyl group; under alkaline conditions, the dichloro ketone hydrates lose hydrogen chloride and pass through the stage of a hydroxide that cannot exist independently, turning into the acids [2].



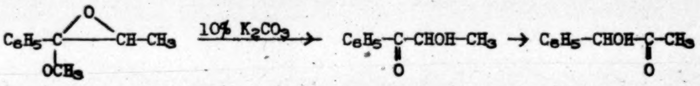
A.E.Favorsky, together with A.Myakotin, V.N.Bozhovsky and M.V.Borodulin [3], showed that it was possible to synthesize saturated acids from the α-chloro and α-bromo ketones. A.E.Favorsky and V.N.Bozhovsky reacted sodium ethylate with α-chlorocyclohexanone in absolute alcohol, and succeeded in obtaining a high yield of an ester, which confirmed the first phase of his hypothesis: the addition of the reagent to the carbonyl group of the halogen ketone [4].

Later, these researches were extended to the halogen aldehydes by S.N.Danilov and E.D.Venus-Danilova, who converted them into saturated acids in a large number of instances. S.N.Danilov and E.D.Venus-Danilova devoted considerable attention to the effect of the reagent upon the course of the isomeric transformation [5]:



In 1941, E.D.Venus-Danilova propounded this general rule: "The greater the alkaline properties of the reagent employed and the higher its solubility in water, the higher will be the yield of acids from halogen ketones and halogen aldehydes."[6]

Reacting aqueous potash with 1-methoxy-1-phenylpropene-1 oxide yielded phenylacetylcarbinol, together with a minute quantity of tar. This apparently takes place in accordance with the following equation:

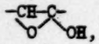


In our previous papers [7], mention has been made of the extremely easy isomerization of methylbenzoyl carbinol to phenylacetylcarbinol in an alkaline medium, which likewise explains the formation of the latter keto alcohol, as we see it, when the oxide is reacted with an alkali.

The keto alcohol was identified by comparing the semicarbazone prepared from the reaction product with the known semicarbazone of phenylacetylcarbinol, as well as by comparison of the glycols produced by their reaction with phenylmagnesium bromide.

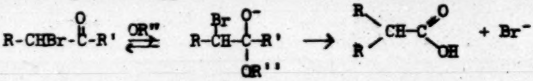
Careful analysis of the product of the reaction between the oxide and the alkali disclosed no trace of an organic acid. We may therefore conclude: the isomerization of halogen ketones to acids does not pass through a stage involving the formation of an alcohol-oxide ring (intramolecular hemi-acetal), but rather the formation of an ester of the acid - via the stage of an ester of the alcohol-oxide (the methyl lactolide of the keto alcohol).

When A.E.Favorsky propounded his hypothesis concerning the formation of "a hydroxide that cannot exist independently" as an intermediate product in the acid transformation of the halogen ketones and formulated this hydroxide as an α-alcohol-oxide



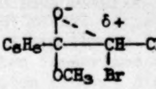
he did not specify the structure of the hypothetical compound completely.

The following equation appears to conform somewhat better to modern theoretical concepts:



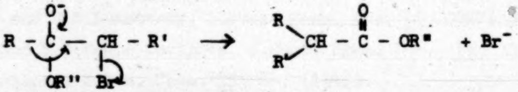
where R'' is a hydrocarbon group or H.

In the compounds produced during the first stage of the process, an ion-dipole reaction may occur between the partially positively charged carbon atoms of the -CHBr- group and the negatively charged oxygen atoms (II):



(II)

Ion-dipole interaction may result in the formation of an oxide ring, but the oxide ring is not rearranged into an ester of the acid. Yet, ion-dipole interaction does not always lead to the detaching of bromine and the formation of an oxide ring; whenever the bromine is active enough, and the reagent present formas a stable bond with the carbon in the carbonyl group owing to its high nucleophilic properties, an electron shift results in the reformation of the carbonyl and the detaching of bromine as a bromine ion, a molecular rearrangement taking place, which gives rise to the ester of the acid:



We are now investigating the carrying out of these reactions along several lines, i.e., defining more accurately the effect of structural factors upon the course of the process when halogen ketones are reacted with nucleophilic reagents.

EXPERIMENTAL

Action of 10% aqueous potash upon 1-methoxy-1-phenylpropene-1 oxide. 7 g of the oxide was added to 100 ml of a 10% aqueous solution of potash. The reaction mixture was heated, with constant stirring, for 1 hour 20 minutes over a boiling water bath. This resulted in a dark-yellow oil settling to the bottom of the flask. The oil was extracted with ether, the ether extract was desiccated with $MgSO_4$, the ether was driven off, and the residue of oil was distilled in vacuum. Double distillation yielded: I - 95-103° (6 mm) - 0.46 g; II - 104-107° (6 mm) - 3.27 g.

Analysis of the 104-107° (6 mm) fraction:

d_4^{20} 1.093; n_D^{20} 1.532; MR_D 42.54; Computed, 41.70.

0.0406 g substance: 11.95 ml CH_4 (14° 767 mm). 0.1115 g substance: 16.5 ml CH_4 (14°, 767 mm) Terentyev and Shcherbakov method). Found: act. H 0.999, 0.93. Computed act. H 1.

The substances reacted at once with semicarbazide. The semicarbazone fused at 182-183° after a single recrystallization from alcohol and exhibited no depression of the melting point when mixed in a test sample with the known semicarbazone of phenylacetylcarbinol, which fused at 187°.

When 1.15 g of the substance was reacted with phenylmagnesium bromide, prepared from 0.75 g of Mg after the usual treatment [7], we got a glycol: 1,2-diphenylpropanediol-1,2, with a m.p. of 95-96°. The glycol exhibited no depression of the melting point when mixed in a test sample with the known glycol prepared from phenylacetylcarbinol, which had the same melting point. The synthesized glycol exhibited the characteristic purple coloring with concentrated H_2SO_4.

SUMMARY

1. It has been shown that phenylacetylcarbinol is formed by reacting 1-methoxy-1-phenylpropene-1 oxide (the methyl lactolide of methylbenzoylcarbinol) with a 10% aqueous solution of potash. A hypothesis is advanced that first methylbenzoylcarbinol is formed, and that it is then isomerized to the more stable phenylacetylcarbinol. Careful analysis of the reaction product disclosed no trace of an organic acid.

2. The equation for the rearrangement of bromo ketones into acids is given.

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*See CB translation p. a-383 ff.

SOME PROBLEMS OF THE THEORY OF ORGANIC CHEMISTRY

(A Discussion Article)

O. A. Reutov

The work of Alexander Mikhailovich Butlerov during the sixties of the past century provided an enduring theoretical foundation for organic chemistry. A characteristic of organic chemistry toward the middle of the past century was the marked lag of theoretical concepts behind the continuous accumulation of extensive factual material. Clearly recognizing that this theoretical lag was retarding the development of the science, Butlerov set about the establishment of a general theory of organic chemistry, based upon all the vast factual material secured by chemists – a theory that was the summing up of the entire development of organic chemistry.

The basic problem, the urgent solution of which was demanded by the imperative tasks facing the science, was this: is the chemical molecule a disorderly pile of atoms, or is the molecule an edifice with a definite arrangement of atoms, with a definite chemical structure?

After analyzing the extensive factual material, Butlerov came to the conclusion that the atoms are bound together in a specific arrangement within the molecule, and that molecules possess a definite chemical structure, which fundamentally governs the properties of a substance. As opposed to Gerard, Butlerov asserted that a chemist who is analyzing a substance can learn the internal structure of the molecule. Not only did Butlerov buttress this materialist assertion with the factual material then available, but he employed the concept of chemical structure he had set forth to make brilliant predictions concerning the existence of a number of then unknown substances which were later synthesized by Butlerov himself as well as by other chemists.

Thus, the doctrine of the order of the atom bonds with the molecule is a component part of Butlerov's theory. But it does not exhaust this theory. Butlerov never reduced chemical structure to the arrangement of the atoms in a molecule. Butlerov's doctrine of chemical structure is much richer and much deeper than such a notion. Butlerov wrote: "At the present time we do not look upon a chemical compound as something dead, motionless; on the contrary, we assume that it is endowed with continuous motion, involving the very smallest particles, whose individual interrelationships are subject to constant change, but add up to some constant mean resultant. We may have constant changes in the chemical particles that make up the mass of the substance, but all this boils down to a known mean state of the mass itself. In a word, we are always faced, in general, by a state of certain mobile equilibrium. This dynamic viewpoint of the nature of a chemical compound and of chemical reactions enables us to provide a clear explanation for phenomena that were completely incomprehensible from the previous point of view...." [1].

It was also Butlerov's achievement to have posed the problem of the interaction among atoms in a fundamental fashion - a problem that is indisolubly bound up with the entire doctrine of chemical structure. He used a number of examples to illustrate the presence of interaction between atoms that are not directly linked to one another, noting, however, that this influence is weaker than in the case of atoms directly linked together. Butlerov wrote the following on this subject: "If hydrogen and chlorine - say, two atoms of each - are linked to an atom of carbon, it actually follows that they are not as dependent upon each other as they are upon the carbon, that there does not exist between them the bond that exists within a particle of hydrochloric acid; in this case, both the chlorine and the hydrogen depend on the carbon approximately as they do in the CH_4 or the CCl_4 particle. But does it follow that there is no relationship between the hydrogen and the chlorine in the compound CH_2Cl_2? I answer this question with a decided negative. On the contrary, a certain relationship doubtless exists between them, even though incomparably less intimate than in hydrogen chloride - a relationship of a different kind" [2].

Further: "There is absolutely no foundation for the reproach leveled at the theory of chemical that in considering the arrangement of the bonds between the elementary atoms in a particle, it leads to the ignoring of the interaction between those atoms that are not directly connected, as it is usually put..."

Thus, there are two sides to Butlerov's theory. One is related to the unconditional recognition of a definite chemical structure in molecules. The other aspect of this doctrine asserts the presence of interactions between atoms, those directly connected together as well as those not so connected.

These two aspects of Butlerov's theory did not develop equally. The large amount of experimental material accumulated by organic chemistry forced chemists to recognize the theory of chemical structure quickly. Most chemists had adopted the doctrine of chemical structure by the end of the last century. At the present time this problem may be considered to be solved in the main. The other side of Butlerov's theory - the problem of the interaction of the atoms within a molecule - developed more slowly, as the pertinent experimental material accumulated. V.V.Markovnikov, a pupil of Butlerov, played a leading part in the development of this problem. With his teacher's theory of structure as his foundation, Markovnikov took the next, extremely important step toward an understanding of the chemical molecule, the interrelationships between its component parts and the effect of these interrelationships upon reactivity. "The problem of the effect of elementary atoms upon the direction taken by the chemical reactions of a compound is one of the most burning questions of contemporary chemistry and, as has been stated above, is attracting more and more attention among chemists. It had to arise, of course, as soon as *most of them had accepted the doctrine of chemical structure* (my italics - O.R.), and is a direct continuation and further development of this doctrine," wrote Markovnikov in his dissertation [3].

Markovnikov used numerous examples to illustrate the presence of interaction between atoms that are directly linked together or are not so directly linked. He used the example of the reaction of the methyl group with the double bond in propyene $CH_3CH=CH_2$, to demonstrate the relation between this interaction and the reactivity of the molecule. These researches resulted in the establishment of the well-known "Markovnikov's rules."

Though the first aspect of the Butlerov theory - the doctrine of chemical structure - was accepted and resolved in principle even during its creator's lifetime, the second aspect of this theory - the doctrine of atom interaction - propounded by Butlerov and Markovnikov could not be resolved during their lifetime. This was chiefly due to the unusual complexity of this problem, its numerous and diversified manifestations, and the abundance of the material accumulating day after day that dealt with this problem.

A large proportion of all the research papers in the field of theoretical chemistry have been devoted to this problem. A number of theories have been advanced during the past four decades in the underlying effort to cope with the material bearing on this problem. They include: A.M.Berkenheim's electronic theory, V.A.Izmailovsky's theory of mesoforms of organic compounds, V.V.Razumovsky's theory of electronic tautomerism, the theory of mesomerism, and several others. The theory of resonance, which we shall discuss in some detail, and which has been widely accepted in recent years, also comes under this heading.

The theory of resonance arose in 1932-1934 as the result of the work of Linus Pauling and his pupils. There were several reasons for the rapid and wide spread of this theory. First of all, it was asserted that the theory of resonance has a rigorous quantum-mechanical foundation and thus is a progressive trend in science, synthesizing physical and chemical ideas. It also seemed that the theory of resonance provided the key to an explanation of a very large group of phenomena in chemistry, and in organic chemistry in particular: the multifarious problems of the structure and the reactivity of molecules. Lastly, some Soviet chemists also manifested an insufficiently critical atitude to fashionable foreign theories as a whole. All these causes combined to make the resonance theory widely accepted in organic chemistry, and partially so in physical, inorganic, and biological chemistry as well. In the Soviet Union the theory of resonance has gained wide acceptance in recent years, this acceptance being largely aided by the researches of Ya.K.Syrkin and his co-workers.

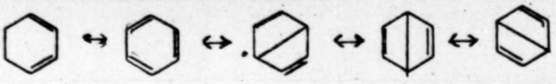
It should be noted that the for a long time apparent successes of the theory of resonance obscured the need for a careful, critical examination of this theory as a whole, including its underlying methodology and its quantum-mechanical foundations. What is more, the analysis of its physical principles involves the greatest difficulty for organic chemists, among whom this theory has found wide acceptance.

In the main, the theory of resonance was designed to describe the electron shell of molecules that could not be described satisfactorily by the classical structural formula alone, employing valency lines. Starting with a formal, approximate computational scheme of quantum mechanics (a linear variant of the method of variations), in which the wave function of the electrons in a molecule is expressed as a series of functions of a system of atoms fairly far apart:

$$\psi_0(x) = \underline{a}_1\underline{f}_1 + \underline{a}_2\underline{f}_2 + \ldots, \tag{1}$$

the theory of resonance proposed to represent such molecules as a collection of "structures" that were in "resonance," thus endeavoring to encompass the experimental material of organic chemistry in a purely formal manner. The function $\psi_0(x)$ represents the electron shell of the real molecule, while the functions $\underline{a}_1\underline{f}_1$, $\underline{a}_2\underline{f}_2$

etc. represent speculative "resonance structures." For example, the structural formula for benzene is described in the theory of resonance as a linear combination of the following five "resonance structures":



(2)

The individual terms of Equation (1) denote the individual structures in (2). It is held that the foregoing structures are "in resonance," resulting in the appearance of an "energy gain," which is responsible for the stability of the benzene molecule, its aromatic nature, and its departure from the additive pattern of organic chemistry.

We shall not spend much time on the quantum-mechanical groundlessness of the basic principle of the resonance theory, referring the reader instead to the papers devoted especially to this problem [4]. In brief this groundlessness involves the following: the functions $\underline{f_1}$, $\underline{f_2}$, etc. in the equation $\psi_0(x) = a_1f_1 + a_2f_2 + \ldots$ applied as a linear variant of the method of variations, define, in the case of benzene, for example, an undisturbed system consisting of non-interacting carbon atoms at an infinite distance from one another. When the carbon atoms approach one another to a distance that is close to or equals the length of the covalent bonds, the individual terms in the function $\psi_0(x)$ (f_1, f_2, etc.) no longer define any states of the real disturbed system, i.e., the real chemical molecule.

Thus, there are no theoretical or experimental bases for identifying the "resonance structures" with any real state of the molecule. A resonance structure is not a physical phenomenon. This concept arose as the result of the incorrect treatment of one of the approximative quantum-mechanical methods of computing molecules. No concept of this sort crops up when a molecule is computed, say, by the method of molecular orbits. It is evident that the fundamental postulate of the resonance theory is false. This theory actually has no quantum-mechanical foundation. Pauling himself, apparently realizing the weakness of the quantum-mechanical underpinnings of his theory, found it necessary to advance other arguments in support of the theory of resonance, abandoning scientific argumentation. He writes: "I think a chemist can secure a correct and useful _intuitive_ (my italics – O.R.) understanding of the concept of resonance by studying its application to various problems...." [5]*, and elsewhere: "... The advantage and the importance of the resonance concept in the consideration of chemical problems are so great that the deficiencies entailed by the presence of elements of arbitrariness are of no great importance" (_Ibid_)*. Thus, Pauling is compelled to appeal, on the hand, to intuition, which has never been the decisive factor in the activity of a scientist, and on the other, to the criterion of advantage, or the criterion of convenience. The part played by the criterion of convenience in the theory of resonance has been defined much more clearly by a pupil of Pauling, Welland, who writes: "... the idea of resonance is a speculative concept to a larger extent than other physical theories. It does not reflect any inner property of the molecule itself, but is a mathematical method invented by the physicist or the chemist for his own convenience." [6]*.

The Soviet chemists Ya. K. Syrkin and M.E.Dyatkina differ with Pauling and Wellard on the significance of the theory of resonance, but in so doing they enlarge upon the mistakes made by the American chemists, beginning to make of fetish of this theory, when they declare that: "the resonance of valency structures is not an ad hoc theory, a thought-up hypothesis, but the necessary consequence of the wave properties of the electron "[7]. Such a definition of the theory of resonance can only confuse the reader.

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* This passage has been re translated from the Russian (trans note.).

Thus, the methodological foundation of the theory of resonance is the "principle of convenience," in no way essentially different from the "principle of the economy of thought," which V.I.Lenin characterized as follows: "...the principle of the economy of thought, if it is actually set as 'the cornerstone of epistemology,' can lead to nothing but subjective idealism. It is most 'economical' to 'think' that only I and my sensations exist - there can be no doubt of that once we introduce so absurd a notion into gnosiology" [8]. Any theory whose methodological foundations involve such a "principle" will be an idealistic one and cannot claim to be scientific.

Let us examine what the "principle of convenience" has led to in the theory of resonance. Proposing to depict a molecule, which exists objectively, independent of our consciousness, as a collection of speculative "resonance structures," the theory of resonance then "derives" the physical and chemical properties of the molecule from the properties of these speculative structures. And resonance theoreticians operate with resonance structures as if these structures were real. The formal (and groundless, to boot) interpretation of a computational method of quantum mechanics is passed off as a phenomenon of quantum-mechanical resonance, determining the properties of chemical molecules.

The scientific thinking of the resonance theoreticians may be gathered from the following characteristic examples.

"We can now examine the problem of the effect of resonance upon the physical and chemical properties of molecules," writes Welland. (cf [8], p. 49).

" Resonance itself determines the aromatic properties of benzene," Pauling asserts. (cf [5], p. 133).

Discussing the reactivity of linear polycondensed hydrocarbons, Ya. K. Syrkin and M.E.Dyatkina write: "The number of structures with elongated bonds increases extraordinarily rapidly in this series. This is the major reason for the increase in reactivity and the facilitation of addition reactions" (cf [7], p. 117).

It is obvious that this method of "research," in which the properties of a real molecule are declared to be the result of the number and properties of thought-up structures as well as the effect of a nonexistent "resonance phenomenon," is falacious and unscientific.

Pauling himself complicates and confuses the issue at the end of his monograph, when he writes: "The difficulty involved in the investigation of benzene and other molecules exhibiting electronic resonance consists in establishing an experimental method that would make it possible to distinguish between these structures and could be carried out rapidly enough" (cf [5], p. 413). Thus, Pauling here renounces his infrequent reminders of the unreality of resonance structures, declaring, in essence, that they are real electronic tautomerisms.

This frank point of view contradicts the original positions of the theory of resonance and approaches the views held by V.V.Razumovsky.*

It is evident from the foregoing that the theory of resonance lacks a physical and, more especially, a quantum-mechanical foundation. Its methodological basis bears the marks of an idealistic Machist stamp. *

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*It must be said that V. V. Razumovsky's "theory of electronic tautomerism" does not possess the methodological flaws set forth above. This theory encounters a number of objections of a physical nature however.

Establishing the semblance of an explanation of an extensive group of phenomena in organic chemistry, the "theory of resonance" distracts the attention of chemists from the solution of essential scientific problems, diverting their efforts to the fallacious path of seeking the causes of the chemical structure of molecules and their reactivity in the properties of fictitious "resonance structures" and in the nature of the non-existent phenomenon of resonance. Because of all this, the "theory of resonance" is a brake upon the further development of the theory of organic chemistry and must be excluded from the arsenal of chemists.**

In connection with the exposure of the speculative nature of the theory of resonance, the need arises for a wide re-examination of the contemporary theoretical notions of organic chemistry in order to exclude from them the speculative assertions introduced by the theory of resonance. It is also of extreme importance to set aside and conserve the rational portion of the achievements of organic chemistry theory during the past decades. In our opinion, the rational portion of the achievements of the theory of organic chemistry during the past two or three decades, which are of objective value, consist principally of the development of the second aspect of Butlerov's theory, i.e. the study, development, and interpretation of the concrete data of organic chemistry on the interaction of atoms in the light of electronic concepts. One of the undoubted achievements of the modern theory of organic chemistry is the establishment of certain general propositions concerning the interaction of atoms (and bonds), in consequence of the study of a large amount of experimental data. We shall mention some of these (generally known) propositions merely in order to point out their objective value, no matter what the language in which they have been or will be set forth.

One of these propositions involves an explanation of the nature of the interaction between atoms that are not directly connected together, but are separated by a system of single bonds.

The phenomena related to this problem are quite extensive, though the most characteristic material on this point is the data on the strength of acids and bases. These data consist, for example, of the varying strength of fatty acids when one of the hydrogen atoms in the carbon chain is replaced by F, Cl, Br, I, NO_3, CN, CH_3, etc. It is obvious that these groups, which are not directly attached to the hydrogen in the carboxyl group, do affect it, differently in each individual case. Experimental data show that this effect grows weaker as the chain of intervening atoms grows longer, as is strikingly shown in the series of α-chloro-substituted acids:

	K
$Cl-CH_2-COOH$	$155 \cdot 10^{-5}$
$Cl-CH_2-CH_2-COOH$	$8.5 \cdot 10^{-5}$
$Cl-CH_2-CH_2-CH_2-COOH$	$3 \cdot 10^{-5}$
$Cl-CH_2-CH_2-CH_2-CH_2-COOH$	$2 \cdot 10^{-5}$

In δ-chlorovaleric acid, the dissociation constant is close to that of the unsubstituted fatty acids, where it is $1.35-2 \cdot 10^{-5}$.

This is the sort of phenomenon that has to be explained. This explanation is of

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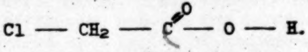
*Also cf footnotes [9] and [10] for a criticism of the philosophical foundations of the theory of resonance

**We shall not deal here with the criticism of the theory of resonance made by G. V Chelintsev. Chelintsev's criticism doubtless helped to draw the attention of the chemical world to this problem. But Chelintsev has made and is still making this criticism from the wrong positions, while the "new structural theory" advanced by him contradicts the experimental facts and the basic postulates of quantum mechanics necessity bound up with the present-day notions of the nature of the chemical bond, according to which a covalent bond is established by an electronic doublet. The Cl–C bond possesses electrical asymmetry, which is manifested, for instance, in the determination of the dipole moment, Cl being the negative end of the dipole. Assuming that this electrical asymmetry is not localized within the confines of the two atoms but is propagated throughout the molecule by an inductive mechanism, as a result of which it becomes easier for the hydrogen of the carboxyl group to be expelled as a proton, we are enabled to explain the foregoing experimental fact, together with an extensive group of other phenomena.

This explanation of the phenomenon might be represented graphically

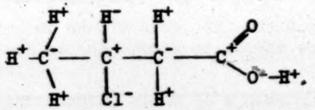
as follows:



$$Cl — CH_2 — \overset{O}{C} — O — H.$$

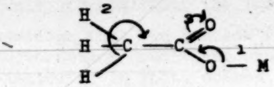
This explanation may undergo changes, of course, as our knowledge regarding the nature of the chemical bond is deepened. Even at present, in many cases, such an explanation does not fully reflect the nature of the interaction between atoms separated by a system of simple bonds. For example, this point of view does not explain why the Cl is much more easily detached as an anion from β-chlorobutyric acid than is the Cl in α-chlorobutyric acid. Nor is it clear why the α-hydrogen atom in α-chlorobutyric acid is readily detached as a proton, while the β-hydrogen atom cannot be. The observed analogy between the behavior of alpha and gamma substituents, on the one hand, and beta and delta substituents, on the other, comes under this heading as well.

An explanation for these phenomena may be found in the notions of alternating polarity propounded by A.M.Berkenheim and Vorlander. This point of view makes it understandable that the release of the β-Cl as an anion and of the α-H as a proton accord with alternating polarity:



In all probability, the road to a deeper comprehension of the multiform nature of the interaction of atoms that are not directly linked together lies in a synthesis of these two concepts of inductive and alternating effects.

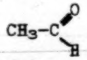
An interesting example of the interaction of atoms separated by a chain of three other atoms is cited in a paper by A.I.Brodksy and his co-workers [11]. They found that in the introduction of deuterium into salts of acetic acid at 150°, the exchange-half-period was nearly 6 days in the case of KM, Na, Ca, and Ba, and only 7 hours in the case of Pb, with Cd and Kg salts occupying an intermediate position. The authors attributed this effect of a metal atom upon the activity of the remote α-hydrogen atoms, most likely correctly, to the competing conjugated M–O and H–C bonds with the carbonyl group:



As the metal in the acetates becomes more electropositive, the 1,3-conjugation increases and the 2,3 -conjugation diminishes, and as a result the hydrogen atoms are less able to detach themselves as protons and to be replaced by the deuterium cation,

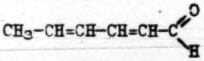
It should be noted that these facts contradict the notion of alternating polarity, since the growth of the partial positive charge on the metal ought to result in an increase in the partial positive charge on the α-hydrogen atoms as well, i.e., in an increase of their activity.. Actual experiments prove that this is not so.

Numerous researches have been carried out in recent years on the transmission of atomic interaction via conjugated double bonds (-CH=CH-CH=CH-...). It has been found that such systems transmit the interaction between atoms that are not directly linked together most efficiently. This transfer of interaction is so complete that in many instances the difference between the interaction of atoms directly linked together and those separated by a system of conjugated bonds is largely effaced, as is shown by a comparison of the chemical properties of the respective compounds. For example, the difference between the two aldehydes:



(I)

and



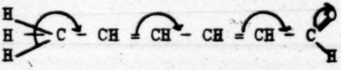
(II)

is that in the first one the methyl group is directly connected to the carbonyl group, whereas it is separated from the carbonyl group by a chain of four carbon atoms in the second one. Nevertheless, the methyl group of the second aldehyde is influenced by the remote carbonyl group just as much as in the first aldehyde. Its hydrogen atoms are mobile, for instance, and aldehyde (II) [like aldehyde (I)] can be condensed as follows:

$$R-CHO + CH_3-CH=CH-CH=CH-CHO \longrightarrow R-CH=CH-CH=CH-CH=CH-CHO.$$

Similarly, the esters of sorbic acid, $CH_3-CH=CH-CH=CH-COOR$, can be condensed at the ω-hydrogen atoms, just as the esters of acetic acid, CH_3-COOR, can be condensed at the α-hydrogen atoms.

This striking phenomenon, which is a common occurrence in organic chemistry, sometimes called vinylogy, consists of the system CH=CH-CH=CH-... behaving like a single unit, transmitting the interaction of the atoms, instead of like an aggregate of isolated double bonds.* The graphic representation of this phenomenon adopted at the present time:



endeavors to mirror the experimental facts known to us: the influence of the carbonyl group upon the methyl group, resulting in "activating" the hydrogen atoms of the methyl group; the semi-disconnected nature of the carbonyl group's π bonds; and, lastly, the fact that the system of conjugated bonds is not a collection of isolated double bonds, but a unit, transmitting the interaction between atoms.

It is common knowledge that the benzene ring, in its unexcited state, does not contain a system of alternating double and single bonds. All the C-C bonds of the benzene ring are equivalent. In fact, doubts sometimes arise as to the justification for the use of the rules for conjugated bonds as applied to the orientating effect of substituents, the reactivity of aromatic compounds, etc. This question deserves some attention. It is an experimental fact that including a benzene ring in a conjugated

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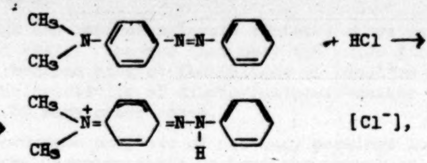
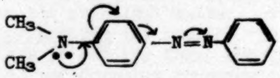
There are also exceptions to this rule to be sure. Cinnamic acid and ω nitrostyrene, for example, are substituted at the ortho and para positions of the benzene ring when acted upon by electrophilic reagents, instead of at the meta position.

system in no way upsets the characteristic property of this system; the transmission of atomic interactions. Moreover, in very many instances, the benzene ring itself behaves like a system of conjugated bonds. This is true, for example, in the reaction of dimethylaminoazobenzene with an acid:



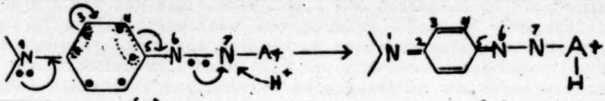
as well as in many other instances. Here the hydrogen ion is not added to the nitrogen in the dimethylamino group, which possesses a free electron pair, but to the ordinarily weakly basic nitrogen in the azo group. In this case, therefore, the reaction center [*] is transferred from the amino nitrogen to the nitrogen in the azo group, although these two atoms are separated by a chain of 5 other atoms. [**] This phenomenon is represented graphically as follows:

(I)



It is probable that this electron shift occurs principally at the instant of the reaction.

For a more rigorous interpretation of this phenomenon the system of conjugated bonds in the benzene ring must be replaced by six π electrons (one per C-atom). It is easy to see, however, that even then the application of the rules of the transmission of influence via a system of conjugated bonds to the benzene ring holds good. In fact, let us consider the system (III), produced by the addition of a proton to dimethylaminoazobenzene, comparing it with the original (II).



(II) (III)

The right-hand benzene ring remains unchanged; hence, the proton is added to the nitrogen (7) at the expense of two electrons of the -N=N- group. When this is so, the electron pair required for establishing the C=N (5,6) double bond comes from the benzene ring (the π electrons 4 and 5), which then acquires a quinoid structure.

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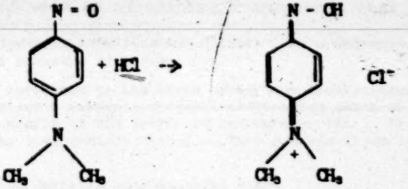
[*] We borrow this term from A. N. Nesmeyanov.

[**] A striking example of the interaction of nitrogen with hydrogen across a benzene ring is seen in the reaction of nitrosodimethylaniline with an acid:

where the reaction center is transferred from the basic nitrogen of the diethylamino group to the oxygen, whose basic properties are usually extremely weak.



The double bond 3,4 in System (III) can then be formed only from the π electrons 2 and 3, while the N=C (1,2) double bond can be formed only from the free electron pair of the amino nitrogen.

Thus, although the benzene molecule contains a system of evenly distributed π electrons while at rest,* changes that obey the rules for conjugated double bonds take place in the benzene ring at the instant of reaction. Hence, the graphical interpretation of the reactivity of dimethylaminoazobenzene (I) is not unjustified. This is also true of many other cases.

We have touched upon only two of the many problems in contemporary organic chemistry.** Still, these examples indicate that the theory of organic chemistry has achieved significant successes during the past few decades, many of which have become part of the permanent treasury of the science.

We must also spend some time upon the problem of representing the molecule. To begin with, we can by no means agree with those scientists who consider this to be a paramount, basic problem, even dividing chemists into different parties, depending upon what method of representation they advocate. This problem has been and remains of minor importance. In his day, A.M.Butlerov clearly stressed this point, writing: "After having set down the principal matters, it will not be superfluous to say a few words now on a minor problem (my italics - O.R.) - the writing of formulas. It is obvious that what matters is not the form, but the essence, the conception, the idea, and bearing in mind that the formulas denoting isomerism must logically express the actual particles, i.e., certain chemical relationships existing in them, it is not hard to realize that any method of notation may be good, provided it expresses these relationships conveniently." [12].

Inasmuch as this statement of Butlerov's is often cited during discussion of the problem of representing molecules, we must deal with it in some detail. The fact is that it contains an error, which may be harmful if it is erected into a principle. The error involves the use of the dubious criterion of convenience for the representation of molecules.*** Here Butlerov touches upon the general problem of the relationship between an object and its representation. The criterion of "convenience" introduces an element of subjectivism into this problem. Various chemists, for instance, may consider the most divergent methods of representation convenient, including those in which the formulas will have only the remotest resemblance to the real molecules. Using the principle of convenience as a guide in the representation of molecules may easily end up in the symbol and the hieroglyphic, i.e., introduce a wholly unnecessary element of agnosticism into molecular representation. To be sure, a representation can never be wholly comparable to the model (the object), but it must mirror it correctly, conveying the objective properties of the model. Thus, the method used for writing formulas must be such that these formulas possess a resemblance to the represented chemical molecules, duplicating to a certain extent (depending upon the level of our knowledge of the molecule) the relationships existing in the molecule.

At the present time, two methods of representation have been proposed for representing molecules of aromatic compounds, as well as of aliphatic compounds that possess conjugated double bonds or double and single bonds, etc. One of these methods depends on the feasibility of representing a molecule (in its major outlines) by means of a single structural formula, with the valency lines supplemented by curved arrows to denote electron shifts:

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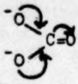
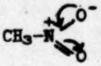
*We shall ignore the fact that the benzene ring in dimethylaminoazobenzene differs from a molecule of benzene in not possessing a perfectly symmetrical envelope of π electrons.

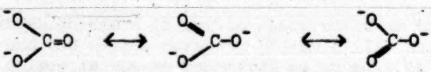
**In discussing these problems we have not committed ourselves to the views of any one theoretician including Ingold's theory of mesomerism, which requires a separate critical examination (such as the problems of unexcited structures, the specific source of the energy of mesomerism, etc.) We have endeavored to consider the factual data and the laws deduced therefrom that possess objective value.

***This error, however, in no way involves Butlerov's underlying gnosiological views.





The other method, which is employed solely in the theory of resonance, involves the representation of the molecule by means of several structures. It should be noted that the employment of such a method of representation is not of itself, a symptom of the methodological errors inherent in the theory of resonance. Organic chemists sometimes employ this method to describe a real molecule, clearly recognizing that none of the individual structures represents any state of the molecule; the molecule is described by the aggregate of these structures. Thus, the following representational method is used for the foregoing carbonate ion:

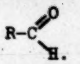


instead of the representation using curved arrows

The method endeavors to convey the experimentally established fact that the carbonate ion is symmetrical. The double-ended arrows (unless commas or dots with commas are used instead) are intended to stress merely the fact that the carbonate ion is represented by the combination of all three of these structures. Obviously, this method of representation cannot give rise to methodological objections of the sort advanced against the theory of resonance as a whole, unless fictitious concepts of the reality of these structures, of their resonating, of an energy gain, etc., are introduced into the representational method. Thus the road from such a method of representation to Machism will be just as long as from the method of representing a molecule by a single structure, since Machism involves a rejection of objective reality (the reality of the molecule), and not one or another representation of objective reality.

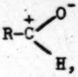
The multistructural method of representing a molecule has basic disadvantages, however. One of them is, for example, the fact that the real molecule, with its definite arrangement of bonds, is often lost (as in the case of naphthalene) behind the multifarious structures, which endeavor to account for the interactions between atoms that are not bound together chemically. As a result, the very concept of chemical structure may often be lost. Moreover, the absence of a rigorous criterion governing the choice of structures results in their aggregate describing not only the basic, characteristic features of the molecule, but also its minor ones, and not even all of them, but only some, chosen arbitrarily. These deficiencies compel us to prefer the method of representing the molecule by a single formula, conveying the major features of the molecule's structure.

The employment of two or a few structures will in some instances, however, constitute a step toward the establishment of a single rational formula. Let us make this clear by way of some examples. Suppose we have to decide upon the structure of an aldehyde group. We draw upon the physico-chemical data for this purpose, say, the dipole moments. We know that nearly all the aliphatic aldehydes have the same dipole moment of about 2.7 debyes, no matter how long their carbon chains. This can only mean that the dipole moment belongs almost exclusively to the carbonyl group:



$R-C(=O)H$ (I)

When we examine the classical formula for an aldehyde (I), we readily see that a molecule possessing such a structure would have a dipole moment that is only slightly greater than one debye. The question arises: can the structure of aldehydes be best expressed in such a case by the formula (II)

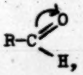


$R-\overset{+}{C}(-O^{-})H$ (II)

where the pair of π electrons is attached wholly to the oxygen atom ? As a calculation of the dipole moment shows, this formula is likewise unsatisfactory in representing the structure of aldehydes; if aldehydes had such a structure, their dipole moment would be approximately 5.7 debyes.

Thus, the aldehyde molecule is not so constructed as to make both of the bonds between the carbon and the oxygen covalent (Formula (I), though the π bond between the carbon and the oxygen is not so polarized as to make it ionic (Formula II). Neither Formula (I) nor Formula (II), by itself, reflects the structure of the carbonyl group quite satisfactorily. They merely circumscribe this structure, "bracketing" it as in artillery fire.

Lastly, we shall take a final step along the road toward establishing a single structural formula for a substance: the correct structural formula for an aldehyde will be one that reflects the partial shift of the π electrons (partial polarization of the π bond). This is usually represented as follows:



$R-C(=O)H$

(the curved arrow indicates the direction in which the π electrons are shifted):

Thus, representing a molecule by means of several formulas (in our example, two) is frequently a step on the road to the establishment of a single rational formula for a substance. This road is justified both logically and, in many cases, historically.

In conclusion, let me point out the following. In connection with the exposure of the speculative nature of the theory of resonance, Soviet chemists face a number of important tasks involving the further development of the theory of chemical structure. Some of these jobs must be handled together with the theoretical physicists. For example, we have to provide a correct interpretation of the results of the application of quantum mechanics to the problems of the theory of chemical structure, and to devise more accurate methods for computing molecules.

The theoretical discussions that have been going on for some time in the chemistry faculty of Moscow State University, in the Institute of Organic Chemistry of the USSR Academy of Sciences, and elsewhere, have made a major contribution to solving moot points and to the establishment of a common viewpoint of Soviet chemists on the basic problems of chemical theory.

Such a method of solving disputed problems is quite essential; it assists in establishing an advanced chemical theory and thus in the successful development of Soviet organic chemistry as a whole.

We can hardly agree with the proposal, put forward by some chemists, for the use of dotted lines to represent molecules in the general case. The use of dotted lines might be justifiable only in the case of perfectly symmetrical molecules and ions such as benzene or the carbonate anion. In the case of naphthalene, however, where the α β and the β β bonds are not equivalent, a dotted line offers no advantage over the classical formula of Erlenmeyer.

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THE FORTHCOMING CONFERENCE ON THE THEORY OF CHEMICAL STRUCTURE

The attention of the chemical world has recently been focused on a critical examination of the present state of the theory of chemical structure. In this connection, the Bureau of the Division of Chemical Sciences of the USSR Academy of Sciences has convoked a Conference on the Theory of Chemical Structure, to be held in Moscow in March, 1951.

The Bureau of the Division of Chemical Sciences of the USSR Academy of Sciences has set up a commission, with the following membership, to prepare the major report at this conference: Academician A.N.Nesmeyanov, chairman; V.N.Kondratyev, coresponding member of the USSR Academy of Sciences, vice-chairman; I.L.Knunyants, corresponding member of the USSR Academy of Sciences; and Prof. V.V.Korshak. This commission has invited many scientists in various fields, working in institutions of higher learning and in research institutes, to participate in its work.

The commission's report will deal with the following fundamental problems:

1. A.M.Butlerov's theory of chemical structure and its further development.
2. A critique of the theory of resonance.
3. The paths of future development of the theory of chemical structure.

The commission's report will be printed and sent to all participants in the conference before it opens. A discussion has been opened on the conference topics in the pages of the following chemical journals: General Chemistry, Physical Chemistry, and Izvestia of the USSR Academy of Sciences, Division of Chemical Sciences.

The commission invites all those interested in the problem of chemical structure to take an active part in the conference.

It is requested that projected theses be forwarded to the commission, c/o the Division of Chemical Sciences, USSR Academy of Sciences, Bolshaya Kaluzhskaya 31, Moscow.